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Powering Advances in Next-Generation Photovoltaics through Materials Synthesis and Characterization

Christie L.C. Ellis
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POWERING ADVANCES IN NEXT-GENERATION PHOTOVOLTAICS
THROUGH MATERIALS SYNTHESIS AND CHARACTERIZATION

A Dissertation Presented
by
CHRISTIE L.C. ELLIS

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 2020

Department of Chemistry
POWERING ADVANCES IN NEXT-GENERATION PHOTOVOLTAICS
THROUGH MATERIALS SYNTHESIS AND CHARACTERIZATION

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by

CHRISTIE L.C. ELLIS

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Kevin Kittilstved, Member

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Ashwin Ramasubramaniam, Member

Ricardo Metz, Department Head
Department of Chemistry
DEDICATION

To my best friend and husband, John, who has been my rock through this experience and has enabled me to accomplish more than I ever thought possible

To my sister, Robin, who has gained twice as much wisdom as me in two fewer years of life and, fortunately for me, is generous in sharing it

To my mentor, Joelle, who helped me find purpose, meaning, and joy in this experience when I couldn’t find it myself
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There have been so many people who have contributed in so many ways, big and small, to allow me to reach this point. I could never acknowledge all of them, or all of the things they’ve done, but here are some of the highlights.

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I would like to acknowledge my wonderful thesis committee. Kevin Kittilstved, who asked the most thought-provoking questions, always built me up, and is one of the
people actively working to make our department a better place for students. Mike Barnes, who has believed in me since I first got to grad school and whose teaching took me from someone who felt they weren’t a capable physical chemist to someone whose physical chemistry-filled work is laid out in the following pages. And Ashwin Ramasubramaniam, who happily made time for me whenever I had questions and whose enthusiasm for my work was energizing and inspiring.

I would like to acknowledge my mentor and friend Joelle Labastide. I have never had such a true role model. I aspire every day to be even half the amazing scientist and person that she is.

I would like to acknowledge my family, who, despite not always knowing what I was doing or why I was doing it (who would sign up for that many more years of school?) were my biggest supporters. They, more than anyone else, know how far I’ve come and what I’ve gone through to get here. My parents, Gayle, Richard, and Diana, and my siblings, especially my sister Robin, all cheered me on from afar. I was also fortunate to have my father-in-law and mother-in-law Bill and Elaine here close to home to support and encourage me.

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I would like to acknowledge the UMass administrators, especially Tricia Serio and Anna Branch, who took our efforts to make this campus a safer place for women seriously in a way I never expected from people at their level. They took countless hours to work with us as equals and give us a seat at the table for discussions which could actually impact the campus.

I would like to acknowledge AAAS and the St. Louis Post-Dispatch newspaper, especially my editor Lisa Brown, who gave me the chance of a lifetime through the AAAS Mass Media Fellowship. This experience grew my writing and communication skills tenfold and launched me into a career path I couldn’t have pursued otherwise.

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Last, and most of all, I would like to acknowledge my best friend and husband, John. He brought me happiness even at my lowest points. He never doubted my ability even when I did. He worked every day to keep me healthy in mind, body, and spirit. He listened to me talk about my research so much that he was practically a collaborator by the end, helping me overcome some of the biggest challenges in my research. This was by far and away the most difficult thing I’ve done in my life and I would not have been able to do it without him.
ABSTRACT

POWERING ADVANCES IN NEXT-GENERATION PHOTOVOLTAICS
THROUGH MATERIALS SYNTHESIS AND CHARACTERIZATION

FEBRUARY 2020

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Directed by: Professor Dhandapani Venkataraman

Solar energy is our most abundant natural resource: the energy from sunlight that
strikes the Earth in one hour is more than the energy consumed globally in a year. This
makes photovoltaics, which convert solar energy into electrical energy, a critical
technology to pursue. 95% of the photovoltaic market is dominated by silicon; its high
efficiency, stability, and plummeting manufacturing costs made it the clear choice for
commercialization. However, silicon solar cells are thick, heavy, opaque, and rigid,
limiting potential applications. They are energy- and resource-intensive to produce, and
their manufacturing process uses and produces several toxic substances.

“Next-generation” photovoltaic technologies have tried to compete with silicon,
boasting improvements in efficiency, stability, toxicity, cost, weight, and benefits such as
semi-transparency or flexibility. Thus far, none of these technologies have surpassed
silicon as each has encountered unique roadblocks. I worked to identify and overcome
these roadblocks for two promising next-generation photovoltaic technologies:
nanoparticle organic photovoltaics (NP-OPVs) and hybrid organic–inorganic perovskites
(HOIPs).
Organic photovoltaics (OPVs) are remarkable for their tunable properties, cheaper synthesis, and thin, flexible, lightweight, semi-transparent devices, opening up applications unavailable to silicon cells. However, after decades of development, OPVs lag far behind silicon in efficiency. NP-OPVs are a subset of OPVs which use organic nanoparticle building blocks for eco-friendly fabrication out of water and greater control over material assembly. Currently, NP-OPVs lag even farther behind their OPV counterparts in efficiency. I investigated device characteristics of NP-OPVs to help close the efficiency gap with OPVs and identified a unique application – indoor power generation – for which OPVs and NP-OPVs are uniquely suited.

HOIP photovoltaics emerged in the last decade and skyrocketed up to efficiencies competitive with silicon. Like OPVs, they have tunable properties, cheaper synthesis, and can be thin, lightweight, flexible, and semi-transparent. Stability is the major roadblock to HOIP commercialization; these devices break down under light, heat, humidity, and applied bias. I built a comprehensive map of how electronic and ionic charge carriers move in response to light, bias, and degradation, and synthesized HOIP derivatives which showed substantial increases in stability under light while maintaining their desirable properties.
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CHAPTER 1
INTRODUCTION

1.1 Current Photovoltaic Market and First-Generation Technology

Photovoltaics (PV) – also known as solar cells – convert energy from sunlight into usable electrical energy, and are one of our most promising sources of alternative energy.\(^1\) The energy from sunlight that strikes the earth in just one hour is more than the total amount of energy consumed globally in a year.\(^2\) Falling manufacturing and installation costs for PV modules have allowed us to begin harnessing this opportunity in earnest, as the average price of a completed PV system has fallen by 59\% in the last decade.\(^3\)-\(^4\) In 2014, solar energy accounted for just 0.7\% of the energy generated in the United States; by 2018, that had more than tripled to 2.3\%.\(^5\) Solar is also one of the most rapidly growing renewable energy sources. In the same five-year period, the percent of all renewable energy generated in the US that came from solar energy sources also nearly tripled, from 4.6\% to 12.9\%.\(^5\)

![Figure 1: A rapidly growing percentage of energy generated in the United States is coming from solar sources.\(^5\)](image)

\(^1\)\(^2\)\(^3\)\(^4\)\(^5\)
A single solar cell technology currently accounts for 95% of the market share of PV production: silicon. First demonstrated in a solar cell in 1954, silicon is a mature “first-generation” technology whose high efficiency, low cost, and long-term stability have enabled its dominance in the PV market. However, there is still substantial room for innovation. Efficient silicon solar cells are thick and heavy, limiting their power-to-weight ratio. They are also rigid and opaque, limiting potential applications where flexible or semi-transparent solar cells are called for. Their manufacturing process is energy- and resource-intensive and produces byproducts which can be harmful to the environment and factory workers. Part of the reason costs have fallen to their current level is the migration of silicon PV manufacturing to China, where waste disposal and worker safety standards are not as high.

Since the advent of silicon, several PV materials have emerged to try and compete, collectively known as next-generation photovoltaics. Different next-generation technologies offer advantages over silicon in terms of efficiency, stability, toxicity, manufacturing costs, and qualitative benefits such as flexibility or semi-transparency. However, each of these materials faces unique challenges to become a true competitor for silicon. In my research, I worked to identify and overcome such challenges in two promising next-generation photovoltaic materials: organic nanoparticles and hybrid organic-inorganic perovskites.

Organic nanoparticle photovoltaics (NP-OPVs), discussed in section 1.3, are a subset of organic polymer/small molecule photovoltaics (OPVs). OPVs offer lower cost synthesis, tunable properties, and the ability to make lightweight, flexible, semi-transparent devices, opening up new applications unsuitable for silicon. NP-OPVs aim to
improve further upon OPVs through a greener and more reliable synthetic process.\textsuperscript{14-15} The major barrier for both OPVs and NP-OPVs is efficiency; in several decades of research, they still lag far behind in this metric compared to silicon and other next-generation technologies.

Hybrid organic-inorganic perovskites (HOIPs), discussed in section 1.4, are one of the newest and most exciting next-generation technologies.\textsuperscript{16-18} In just a decade of development, they offer efficiencies competitive with commercial silicon solar cells. Like OPVs, they offer lower cost synthesis, tunable properties, and the ability to make lightweight, flexible, semi-transparent devices. The major roadblock for HOIPs is their instability, especially under light.\textsuperscript{19-21}

In Chapter 2, I identify indoor power generation as a promising application which NP-OPVs and HOIPs may already be better suited to than silicon. I highlight how the common conflation of the terms “photovoltaic” and “solar cell” has caused these materials to be overlooked for such applications and demonstrate their superior performance under LED light compared to silicon. In Chapter 3, I investigate the loss in voltage in NP-OPVs compared to their OPV counterparts. I identify charge-trapping and poor extraction at the cathode interface as the cause of this phenomenon and propose solutions to close this gap. In Chapter 4, I disentangle the effects of light, bias, and degradation on electronic and ionic charge carriers in HOIP photovoltaic devices and present a comprehensive scheme describing ion transport under these varying conditions. In Chapter 5, I present newly synthesized HOIP derivatives which show improved stability under light through substitution of the organic cation with larger molecules. I identify and quantify a novel autocatalytic degradation mechanism and discuss trends in
structure and kinetics in relation to molecular properties. In Chapter 6, I discuss prospective future directions to build on my research.

1.2 Photovoltaic Device Operation and Evaluation

Photovoltaic active materials are semiconductors that are able to convert energy from light into electrical energy.\(^{22}\) When these materials are exposed to light, a photon is absorbed which excites an electron from the valence band into the conduction band, leaving a hole behind. These free electrons and holes can then be used to generate a current by differentially extracting holes at one side of the photovoltaic device and electrons at the other side. To accomplish this in a full photovoltaic device (illustrated in Figure 2b), an electron transporting layer (ETL) is placed on one side of the active material and a hole transporting layer (HTL) is placed on the other side. The ETL has an energy level which aligns with the conduction band of the active material, allowing electrons in the conduction band to move into this layer but blocking holes. Conversely, the HTL energy level aligns with the valence band, allowing holes to move through but blocking electrons. On the outside of the ETL and HTL are conducting electrodes to extract these charges. At least one of these electrodes and the ETL/HTL beneath it must be transparent to allow sunlight to reach the photovoltaic active material. The transparent electrode most commonly used in PV devices is indium tin oxide (ITO). The electrode on the opposite side is typically a metal. An actual OPV device made in our lab is shown in Figure 2c, with the top metal electrodes and the purple-colored organic active material visible.

The primary metric for comparing PV devices is power conversion efficiency (PCE), which describes how efficiently a device is able to convert energy from light into
electrical energy. The theoretical maximum of PCE for a PV device in sunlight, known as the Shockley-Queisser limit, is 33.7%.\textsuperscript{23} Silicon has a current record PCE of 27.6%.\textsuperscript{24} HOIPs are quickly approaching this value, with a current record PCE of 25.2%. While significant strides in OPV efficiency have been made in the past three years, the record PCE for an OPV is still only 17.4%.

PCE is measured by applying a varying voltage ($V$) to a PV device and measuring the current density ($J$) output. This results in a $J$-$V$ curve such as that in Figure 2a. The y-intercept of this curve is known as the short-circuit current ($J_{SC}$), the x-intercept is known as the open-circuit voltage ($V_{OC}$), and the squareness of the curve is known as the fill factor ($FF$). These three factors multiplied and then divided by the input light power give the PCE. Each of these values can give insight into the physical processes occurring in a device.

![Figure 2](image)

**Figure 2:** (a) How PCE is calculated based on $J$-$V$ measurements of a PV device. $V_{OC}$, $J_{SC}$, and $FF$ give specific information about different aspects of device performance. (b) Architecture of a PV device (side slice view). ETL = Electron transporting layer, HTL = hole transporting layer. Organic nanoparticles and HOIPs both act as the active material. (c) Top view of an actual OPV device.
1.3 Nanoparticle Organic Photovoltaics (NP-OPVs)

1.3.1 Organic Photovoltaics (OPVs): Advantages and Challenges

Organic photovoltaic (OPV) materials are semiconducting polymers or small molecules, a huge variety of which have been used in these devices before.\textsuperscript{1, 13, 25} Unlike silicon, they can be fabricated from solution, which decreases manufacturing costs significantly using processes like roll-to-roll printing.\textsuperscript{26-27} They can be made very thin, lightweight, semi-transparent, and flexible, opening up a plethora of applications unsuitable for thick, heavy, opaque silicon cells, such as solar windows, solar fabrics, solar paints, and flexible electronics. The variety of available materials allows ample opportunity to tune everything from functional properties to aesthetic properties like color.

The first OPV was created by C.W. Tang at the Eastman Kodak company in 1986,\textsuperscript{28} and research advances in polymer synthesis and solution processing in the 1990s turned OPVs into a rapidly growing field.\textsuperscript{13} However, in more than three decades of development, their record PCE is still only 17.4%: not high enough to compete with silicon.\textsuperscript{29} Additionally, the highest efficiency materials are often expensive due to complex, multi-step syntheses. There have been attempts to commercialize OPVs, but these have largely been unsuccessful.\textsuperscript{30-32}

OPVs require a mixture of two different organic materials: an electron transporting material (ETM) and a hole transporting material (HTM) (also referred to as an electron acceptor and electron donor, respectively).\textsuperscript{27} There are strict bounds on the morphology of this mixture which will give an efficient OPV.\textsuperscript{15, 33-34} When organic materials absorb a photon and promote an electron, the newly generated electron and hole
remain bound to one another, forming an exciton. In order to transport the electrons and holes to opposite ends of the device, the electron and hole in the exciton must be separated. This happens at the interface between the ETM and HTM. Therefore, it is crucial to the function of OPVs that the two materials have interfacial contact, with domains of each material in between that are no larger than the distance an exciton can travel (on the order of $10^1$ nm). However, once the electron and hole are separated, they also need a continuous pathway of either the ETM or HTM to the electrodes.

This desired higher-order structure which balances interfacial contact area and continuous nanosized pathways is known as a bulk heterojunction (BHJ) morphology, illustrated in Figure 3. This is a critical roadblock in development of new OPV materials, as formation of the higher order structure in a polymer/small molecule mixture can be drastically affected by a number of factors such as intermolecular interactions, crystallization rates, solvent evaporation rates, and temperature. Thus, any time even small changes are made to the ETM or HTM, the process to form the desired BHJ often has to be optimized from scratch, extending the research time for new materials substantially.

Two of the most extensively studied OPV materials, poly-3-hexylthiophene (P3HT, a hole-transporting polymer) and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{60}$BM, an electron transporting small molecule), are known to form this BHJ structure (Figure 3). Their record PCE is only 6.5%, but they provide a useful model system to understand the mesoscale assembly of organic materials. As illustrated in Figure 3, the ideal BHJ structure has crystalline domains (the continuous pathways to the electrodes) as well as amorphous domains (the interfacial contact area for separating excitons).
However, alternative undesirable mesoscale morphologies can also form, such as a single phase, fully-mixed structure, where interfacial contact is maximized but no continuous pathways exist, or a phase-separated structure, where there are large continuous domains but minimal interfacial contact.

Figure 3: Formation of the bulk heterojunction (BHJ) mesoscale architecture necessary for optimal organic photovoltaic (OPV) function illustrated with two common OPV materials, P3HT (a hole conducting polymer) and PC₆₀BM (an electron conducting small molecule). Formation of this structure is dependent on the interplay of a variety of factors such as crystallization rates, intermolecular interactions, solvent evaporation rate, and temperature. In non-ideal conditions, OPV materials may form alternative mesoscale morphologies, such as the fully mixed one phase or the fully separated two phases.

1.3.2 Nanoparticles as an Alternative Synthetic Route to OPVs

Nanoparticle OPVs (NP-OPVs) have emerged as a promising solution for the challenge of controlling mesoscale assemblies in OPV active materials. They separate the two requirements for a BHJ morphology – the crystalline nanosized domains
and the interfacial contact area – and form each individually in sequential steps. The nanoparticles themselves serve as the crystalline domains; since nanoparticle size can be controlled during synthesis, this domain size can be easily tuned. Nanoparticles of the desired ETM and HTM can be formed separately, with different domain sizes if desired. Then, the ETM and HTM nanoparticles are mixed and assemble via sphere packing, leading to a predictable amount of interfacial contact area. The nanoparticle method allows the domains to assemble geometrically, eliminating the complicating effects of intermolecular interactions that can lead to too much mixing or phase separation. The ratio of ETM to HTM can also be tuned by simply mixing different amounts of the two nanoparticles.

**Figure 4:** Comparison on different length scales of conventional organic film formation vs nanoparticle-controlled film formation.\(^1^5\)
Nanoparticles are synthesized using a mini-emulsion method, whereby a solution of the OPV material dissolved in an organic solvent is sonicated with an aqueous surfactant solution. The sonication gives droplets of organic solution \( \sim 10^1 - 10^2 \) nm in diameter surrounded by surfactant. Then, the organic solvent is evaporated and the organic material within the droplet aggregates, giving nanoparticles of the organic polymer or small molecule surrounded by surfactant and suspended in water. This method is compatible with the majority of OPV materials, as the only requirement is that the material be soluble in an organic solvent. Nanoparticle size can be tuned over a range of 30-180 nm in diameter by changing the surfactant concentration, organic solvent, water to organic solvent ratio, and sonication power.

A major advantage of the NP-OPV method is that the active material films can be processed from water, rather than the toxic chlorinated solvents typically used for OPVs. Approximately 16 million liters of chlorobenzene is needed to fabricate 1 GWp of traditional OPVs, so the ability to use water for this manufacturing process instead will have a substantial environmental impact.

### 1.3.3 Outstanding Challenges in NP-OPVs

Despite their advantages, NP-OPVs have not been able to match the efficiencies of their BHJ OPV counterparts, which already suffer from PCEs too low to be commercially competitive. Therefore, for nanoparticles to be an effective tool for accelerating OPV research, the factors which lead to a decrease in PCE in the NP-OPVs must be discerned and rectified. Some potential concerns have already been investigated and ruled out. It was hypothesized that the surfactants surrounding the organic nanoparticles would impede charge transport and lead to an overall decrease in
conductivity. However, when the excess solvent from solution is removed, NP-OPV films exhibit efficient charge transport. Therefore, there is a continued need to investigate the device properties of NP-OPVs to determine where they lose efficiency compared to traditional OPVs.

1.4 Hybrid Organic-Inorganic Perovskite (HOIP) Photovoltaics

1.4.1 Advantages and Challenges of HOIP Photovoltaics

Hybrid organic-inorganic perovskite (HOIP) materials, though long known, have exploded onto the research scene and experienced unprecedented growth in fundamental knowledge and practical applications in just a few years. Their unique array of characteristics arising from their combination of organic and inorganic elements makes them a promising platform for applications as diverse as thermoelectrics, piezoelectrics, field effect transistors, lasing, LEDs, memory storage, computing, sensing, and, perhaps most prominently, photovoltaics. They are semiconducting, ambipolar charge transport materials with high electron and hole mobilities. They have long carrier diffusion lengths, low recombination rates, and an easily tunable direct band gap that absorbs the majority of the solar spectrum. They can be fabricated from inexpensive, abundant precursors at low temperature using solution-based processes amenable to commercial fabrication, and form thin, flexible, semi-

transparent films that are ideal for a variety of commercial applications that are
unsuitable for silicon photovoltaics, which are thick, opaque, and rigid.

The long list of accolades for HOIPs is accompanied by a comparable list of
chemical, inorganic lattice distortion and phase transitions, molecular
rotational freedom, spin orbit coupling and relativistic band splitting, unique polaron
nature, ferroelectricity, local domain variations, interface modifications, and transport of
ions must be considered to fully understand its fundamental properties.56-58

1.4.2 Background on HOIPs

The first all-inorganic alkali-metal lead and tin halide perovskites were
synthesized in 1893, and their crystallographic structures were determined in 1958 by
Christian Møller.59-60 Møller also noted that these materials exhibited photoconductivity,
but never fabricated photovoltaic devices. The first hybrid organic-inorganic perovskite
(HOIP), methylammonium lead triiodide (MAPbI3), was fabricated by Dieter Weber in
1978.61 The optoelectronic properties of these materials were investigated in the early
1990s by Mitzi and coworkers, but since their work focused on LEDs and transistors,
photovoltaic devices were never made.62 Instead, HOIPs first emerged in the photovoltaic
community not as a primary active material, but as a light-absorbing dye in dye-
sensitized solar cells (DSSCs). The first liquid hybrid perovskite DSSC was fabricated in
2009 and had a power conversion efficiency (PCE) of 3.5%.63 These materials truly
exploded in 2012, when Grätzel, Park, and coworkers, and Snaith, Murakami, Miyasaka,
and coworkers fabricated solid state HOIP active material photovoltaics using MAPbI3
and MAPbI$_3$Cl$_{1-x}$, respectively, with PCEs of 8-10%, surpassing the best known solid state DSSCs and many of the organic photovoltaic materials at the time.$^{64-65}$ The development in high efficiency HOIP photovoltaics underwent unprecedented progress from this point, culminating in a device with a certified PCE of 25.2% in 2019, which rivals the most efficient photovoltaics available today.$^{66}$

The term “perovskite” refers to a particular crystal structure with stoichiometry ABX$_3$, shown below in Figure 5a.$^{54}$ The most common HOIP materials have an organic ammonium-based A cation (ex: methylammonium (MA), formamidinium (FA)), a divalent metal B cation (ex: Pb, Sn), and a halide X anion (I, Br, Cl). The most commonly studied material in this family is methylammonium lead iodide (MAPbI$_3$). Though Figure 5a depicts the high symmetry cubic perovskite structure, HOIPs can undergo multiple phase transitions and have significant crystallographic flexibility, shown in the powder neutron diffraction pattern in Figure 5b. MAPbI$_3$, for example, is orthorhombic (space group = Pnma) below 165 K when MA$^+$ dipoles are all aligned, undergoing a sharp first-order transition to tetragonal (I4/mcm) at 165 K when MA$^+$ gains some rotational freedom, then undergoing a continuous second-order transition to high-symmetry cubic (Pm$\bar{3}$m) at 327 K, where MA$^+$ ions are fully disordered.$^{67}$ The PbI$_6$ octahedra also undergo significant distortion, even in the cubic phase, contributing to the bulk flexibility of these materials. Additionally, the cuboctahedra can expand and contract significantly.
Figure 5: (a) Typical cubic HOIP crystal structure with ABX$_3$ stoichiometry, where B is the divalent metal cation at the center of the octahedra, X are the anions at the corners of the octahedra, and A is the organic cation in the cuboctahedral cavity. (b) Powder neutron diffraction pattern of MAPbI$_3$ and schematic of MA$^+$ disorder in each phase (Reprinted with permission from Frost, J. M. & Walsh, A. *Accounts of Chemical Research*, doi:10.1021/acs.accounts.5b00431 (2016). Copyright 2016 American Chemical Society).

At 25.2% power conversion efficiency (PCE), HOIPs have already demonstrated that they can compete with the most efficient commercial photovoltaics. In the Shockley-Queisser limit, single-junction HOIPs have a theoretical potential PCE of nearly 30%, which could be exceeded using tandem cell architectures.$^{69-70}$ MAPbI$_3$ devices show a loss-in-potential (difference between bandgap and open circuit voltage ($V_{oc}$)) of only 450 meV, already extraordinarily close to the thermodynamic minimum loss-in-potential of 250-300 meV and better than all but three currently used photovoltaic technologies.$^{71}$

This is one of many indications of the anomalously low electron-hole recombination rates in HOIPs, which persist even in low temperature solution-processed devices, which typically have high bulk defect densities. The band gap of MAPbI$_3$ is already close to ideal for photovoltaic applications at 1.55 eV and has been shown to be easily tunable by doping or substitution with different organic cations or halides. Excitons in HOIPs have very low binding energies of 0.030 eV for MAPbI$_3$, and therefore easily dissociate into
free carriers at room temperature; HOIPs are also ambipolar charge transporters with high
electron and hole mobilities of 7.5 cm² V⁻¹ s⁻¹ and 12.5-66 cm² V⁻¹ s⁻¹, respectively, for
MAPbI₃, and long carrier diffusion lengths of 100 nm - 1000 nm, much longer than the
film thickness needed for full optical absorbance.⁴⁴

1.4.3 Ion Transport in HOIPs

Ion transport has been implicated as the cause of many important properties
associated with HOIPs, yet the chemical identity of the migrating ion or ions and the
mechanism of transport remains unclear. HOIPs, like traditional oxide-based perovskites,
express several experimental hallmarks of ion transport. Nonetheless, studying ion
transport in these materials has not been straightforward due to several factors that
complicate data analysis and interpretation.⁷²-⁷³ First, there are multiple possible mobile
ions in HOIPs, and it is possible that all of them are responsible for the experimental
observations of ion transport (Figure 6a).⁷⁴-⁷⁶ Second, HOIPs are both semiconductors
and ionic conductors; thus, there is a possibility of coupled ionic-electronic transport.
Third, HOIPs are relatively unstable materials; they have a high and variable defect
density and degrade quickly under many device relevant conditions such as light, heat,
humidity, and electrical bias.⁷⁷ Fourth, the non-spherical organic counterions in HOIPs
interact with the lattice framework through a diverse array of supramolecular interactions
such as van der Waals, dipole-dipole, and hydrogen bond interactions. These interactions,
coupled with lattice distortions, phase transitions, grain boundaries, and interfaces,
complicate the interpretation of the experimental data (Figure 6b).⁵⁶-⁵⁸ With several
interconnected and synergistic factors influencing ion transport coupled with a flood of
publications (and data) in a short time span, there is diversity in opinion on the nature of ion transport in HOIPs.

Figure 6: (a) Possible mobile ions in MAPbI$_3$: I$^-$, Pb$^{2+}$, MA$^+$, and H$^+$. (b) Selected possible pathways for ion migration (Reprinted with permission from Yuan, Y. & Huang, J. *Accounts of Chemical Research* 49, 286-293, doi:10.1021/acs.accounts.5b00420 (2016). Copyright 2016 American Chemical Society).

1.4.3.1 Qualitative Evidence of Ion Transport

Structural and electrochemical studies on HOIPs have been a rich source of evidence in support of ion transport. Grätzel, Maier, and coworkers performed a classic solid-state electrochemical experiment under dark conditions on a cell with architecture (cathode to anode) of Pb/MAPbI$_3$/AgI/Ag. Under electrical bias, the formation of PbI$_2$ or MAI at the interface of MAPbI$_3$ with either Pb or AgI would indicate that certain ions were able to move to these reactive interfaces. Based on energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) data, the authors concluded that PbI$_2$ formed at the Pb/MAPbI$_3$, showing that I$^-$ is the fastest moving ion. However, they did not examine the MAPbI$_3$/AgI interface for MAI formation since they did not observe any change at this interface in scanning electron microscopy (SEM) images. This evidence does not conclusively rule out the possibility of mobile MA$^+$ ions. Huettner and
coworkers observed uneven distribution of iodine and lead using X-ray photoemission spectroscopy (XPS) in a micron-sized MAPbI$_3$ crystal after the application of electric bias. They observed a range around the ideal I/Pb ratio of 3 with ratios as low as 1 in the center of the crystal and as high as 6 at the cathode.$^{79}$ Additionally, Huang and coworkers have reported several key results in this area; they fabricated a symmetrical horizontal micron-length MAPbI$_3$ device, and observed the movement of a PbI$_2$ “thread” through the film under small applied bias using optical microscopy, EDX, SEM, and XRD (Figure 7).$^{80}$ They reasoned that, for this to occur, both MA$^+$ and I$^-$ had to be mobile and undergo forward and backward reactions in the solid state at comparable rates. They observed the movement of MA$^+$ ions through a MAPbI$_3$ film by photothermal induced resonance (PTIR) under applied bias on a timescale of hundreds of seconds.$^{81}$ They also used XPS and ultraviolet photoelectron spectroscopy (UPS) to demonstrate that changing the stoichiometry of the two MAPbI$_3$ precursors, MAI and PbI$_2$, as well as thermal annealing, could drastically vary the energy levels and p- or n-doped character of the films, as shown in Figure 7.$^{82}$ While this last result does not directly indicate ion movement, it does demonstrate that presence of excess ion species/defects can alter the HOIP energy levels, supporting the hypothesis that ion movement and accumulation is related to $J$-$V$ hysteresis.
Techniques traditionally used to study simple electrically conducting systems have also proven useful for examining ion movement. Huang and coworkers discovered that the photocurrent direction in nearly symmetrical ITO/PEDOT:PSS/MAPbI$_3$/Au devices was switchable with applied bias directions by reversibly doping to either an n-i-p or p-i-n structure as measured by Kelvin probe force microscopy (KPFM).\textsuperscript{83} They attributed this effect to ion movement – speculating that I$^-$, MA$^+$, and Pb$^{2+}$ might be involved – as polarization information could be retained in the film for many months after initial poling, poling was frozen at low temperatures, and reversible color change was observed near cathode and anode after poling. Bisquert and coworkers fabricated a MAPbI$_3$ photovoltaic (PV) device, which they poled in the dark for 30 s with 0, -1, or -2 V, short circuited for 1 min to eliminate electronic charge accumulation, then switched quickly from $V_{oc}$ to $J_{sc}$ conditions and measured time-dependent photocurrent density,
shown in Figure 8.\textsuperscript{84} They observed an initial non-steady-state photocurrent process with a fast decay time in all samples when the bias was switched from $V_{oc}$ to 0 V. Additionally, they observed a second non-steady-state process, where the photocurrent density was initially much lower and recovered to the 0 V value after several minutes in the -1 V poled cell and more so in the -2 V poled cell. They reasoned that this process was too slow to be accounted for by electronic carrier phenomena and instead fit well with reduced band bending due to ion redistribution; additionally, they note that this hysteretic effect cannot be accounted for by ferroelectric band bending, as a voltage $>V_{oc}$ would need to be applied to recover unpoled steady state current in this case. Frost and Walsh further addressed potential causes of observed slow electrical phenomena by demonstrating the similarity of dielectric permittivity measurements of MAPbI$_3$ made by Bisquert and coworkers to a 2008 paper by Lunkenheimer and coworkers.\textsuperscript{72,85-86} Lunkenheimer used banana skin – a known paraelectric ion conductor – to demonstrate that simple dielectric permittivity measurements can differentiate between polarization caused by ion conduction and ferroelectricity; Bisquert’s permittivity measurements, as shown beside those of the banana in Figure 8, have a strikingly similar frequency dependence, with greatly increased permittivity at low frequency corresponding to ion conduction.\textsuperscript{85}
1.4.3.2 Computational Studies of Ion Transport

Computational modeling using density functional theory (DFT) provides a useful tool to independently model multiple phenomena in HOIPs, and thus has been a critical tool in gaining insight into ion transport. Modeling has been used to predict quantitative values such as formation energies of ion-related defects or activation energies of defect/ion migration that could be validated by experiments.

Yan and coworkers calculated formation energies of various defects such as vacancies, interstitials, cation substitutions, and anti-site substitutions for I⁻, Pb²⁺, and MA⁺ in MAPbI₃.⁶⁹ They found that these formation energies were sufficiently low – many <1 eV and as low as 0.2 eV – and predicted that many of these defects are likely present in this material. In addition, they observed that those ionic defects with low formation energies lead to shallow electronic traps. This prediction is consistent with the low non-radiative recombination rates and inconsistent with long time scale (de)trapping.
processes. Following this study, several groups calculated activation energies ($E_a$) for migration of several ionic defects using transition state modeling (see Table 1).

**Table 1: Computationally determined activation energy ($E_a$) values of possible mobile ions by migration mechanism.**

<table>
<thead>
<tr>
<th>Ref.</th>
<th>I (Vacancy)</th>
<th>I (Interstitial)</th>
<th>MA$^+$ (Vacancy)</th>
<th>Pb$^{2+}$ (Vacancy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Islam</td>
<td>0.58 eV</td>
<td>---</td>
<td>0.84 eV</td>
<td>2.31 eV</td>
</tr>
<tr>
<td>Tateyama</td>
<td>0.33 eV</td>
<td>---</td>
<td>0.55 eV</td>
<td>---</td>
</tr>
<tr>
<td>De Angelis</td>
<td>0.16 eV</td>
<td>0.16 eV</td>
<td>0.46 eV</td>
<td>0.80 eV</td>
</tr>
<tr>
<td>Mattoni</td>
<td>0.10 eV</td>
<td>0.24 eV</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Du</td>
<td>0.26 eV</td>
<td>0.19 eV</td>
<td>0.62 eV</td>
<td>--</td>
</tr>
</tbody>
</table>

Islam and coworkers calculated an $E_a$ of 0.58 eV for I- vacancies, 0.84 eV for MA+ vacancies, and 2.31 eV for Pb$^{2+}$ vacancies. They concluded from these numbers, as well as the knowledge that many perovskites are known oxide anion conductors, that iodide is the most likely mobile species while methylammonium and lead are unlikely to be mobile (Figure 9). They also concluded that collection of iodide ions and vacancies at device interfaces could influence the band energies and create hysteresis.

Mattoni and coworkers modeled I- movement through two possible mechanisms – vacancy diffusion or interstitial diffusion. They found a difference in $E_a$ for the two different mechanisms as well as much lower overall $E_a$ values – 0.10 eV for vacancy diffusion and 0.24 eV for interstitial diffusion – indicating that the vacancy diffusion is the preferred ion diffusion pathway. Tateyama and coworkers calculated $E_a$ in both MAPbI$_3$ and FAPbI$_3$ for I- vacancies and MA+/FA+ vacancies along different crystallographic axes (Figure 9). They calculated Ea values for both I- diffusion (0.33 eV) and MA+ diffusion (0.55 eV) that were lower than those calculated by Islam and coworkers. They also found that Ea for formamidinium (FA+) diffusion was comparable to MA+ diffusion (0.57 eV). They criticized the comparison of HOIPs to oxide
perovskites, as oxide conducting perovskites have stronger ionic bonding character. However, both Tateyama and Mattoni note that the $E_a$ values they obtained are well within the ranges of those in known ion transporting materials, suggesting the likelihood that both the halide anion and the organic cation could be mobile. De Angelis and coworkers found lower, identical I- vacancy and I- interstitial $E_a$ values (0.16 eV), a MA+ vacancy $E_a$ value comparable to Tateyama and coworkers (0.46 eV), and a significantly lower Pb$^{2+}$ vacancy $E_a$ than Islam and coworkers (0.80 eV). They reasoned that I- was moving on the scale of ns, too quick to account for the ms/s timescale hysteresis effect, and that mobile MA+ or possibly Pb$^{2+}$ was more likely responsible. Additionally, De Angelis and coworkers performed a density of states (DOS) calculation for a MAPbI$_3$/TiO$_2$ ETL planar interface, and found that accumulation of oppositely charged ions/defects at the interface could cause band bending which could either impede or assist charge extraction, depending on which direction the applied electric field caused ions to migrate. Du and coworkers calculated $E_a$ values for both interstitial and vacancy movement of I- and MA+ in MAPbI$_3$. They found that, while these values were low enough to potentially be occurring, interstitial movement was favored for both. For I-, they calculated a minimum $E_a$ of 0.26 eV for a vacancy pathway and a minimum $E_a$ of 0.19 eV for an interstitial pathway, and for MA+, a minimum $E_a$ of 0.62 eV for a vacancy pathway and a minimum $E_a$ of 0.38 eV for an interstitial pathway.
Rappe and coworkers calculated low activation energies for hydrogen movement by the Bourgoin-Corbett mechanism, where hydrogen is able to capture or release free carriers and migrate along the I-Pb-I bond axis as H$^+$/H$^0$/ as it is selectively stabilized by local anionic, neutral, or cationic character.91 Hydrogen migration is not treated extensively in the literature as hydrogen defects are considered to be minor in HOIPs with a predicted concentration of $\sim 10^{11}$ cm$^{-3}$. In comparison, the concentrations of Pb$^{2+}$, I$^-$, and MA$^+$ defects are predicted to be $\sim 10^{17}$- $10^{20}$ cm$^{-3}$. Nonetheless, it is acknowledged that water infiltration into HOIP films may affect these defect concentrations.72
Although computation provides insights into possible mechanistic pathways and activation energy barriers, the prediction to be computationally verified. In the next section, we describe key techniques to measure ion diffusion in solids. We first look at the direct techniques for studying ion diffusion and the limitations of these techniques to probe ion diffusion in HOIPs.

1.4.3.3 Quantification of Ion Transport Activation Energy

Activation energy ($E_a$) measurements have been pursued widely as a way of quantifying ion movement, but the measured values and the assigned ion identities vary. In addition to computational modeling of ion transport, Islam and coworkers employed chronophotoamperometry to determine the lowest activation energy for ion mobility in MAPbI$_3$, and found this $E_a$ to be 0.60-0.68 eV. They concluded that I$^-$ was the mobile ion since their experimental $E_a$ was in close agreement with their calculated $E_a$ (I$^-$) of 0.58 eV, and the mobile ion was likely responsible for $J$-$V$ hysteresis. Huang and coworkers observed two mobile species, termed “fast ions” and “slow ions”, from their PTIR experiments, and calculated an $E_a$ of 0.36 eV for the fast ions. They hypothesized that both these mobile species could be MA$^+$, perhaps moving through different pathways. In another study, Huang and coworkers investigated MAPbI$_3$ using temperature dependent conductivity and found that $E_a$ values obtained under dark (0.08 eV) differ from values obtained under illumination (0.27 eV) in a variety of samples. They concluded that I$^-$ was the mobile ion; additionally, they noted that ion migration was not observed in single crystals over the course of several days. Kingon and coworkers observed two separate thermally activated $E_a$ values, 0.10 eV and 0.41 eV, by temperature-dependent pulsed voltage-current measurements designed to separate
electronic and ionic conductivity, which they assigned to I\(^-\) and MA\(^+\) migration, respectively.\(^\text{93}\) Venkataraman and coworkers used electrochemical impedance spectroscopy (EIS) to determine activation energies using the Warburg element feature present in the spectra of MAPbI\(_3\), MA\(_x\)FA\(_{1-x}\)PbI\(_3\), and FAPbI\(_3\) photovoltaic devices.\(^\text{94}\) They found \(E_a\) values of 0.58 eV below 320 K and 0.23 eV above 320 K for MAPbI\(_3\), 0.63 eV for mixed MA\(_x\)FA\(_{1-x}\)PbI\(_3\), and 0.22 eV below 330 K and 0.79 eV above 330 K for FAPbI\(_3\). The activation energies measured from the Warburg element were attributed to the organic cation transport as there was a change in \(E_a\) upon changing organic cation from MA\(^+\) to FA\(^+\). Also, the measured values were similar to the computed vales for MA\(^+\) transport, and the observed discontinuity in \(E_a\) for MAPbI\(_3\) matched with the phase transition temperature from tetragonal to cubic. Fan and coworkers also used EIS to determine MAPbI\(_3\) \(E_a\), verifying the model used and Warburg element observed by Venkataraman and coworkers.\(^\text{95}\) They found a discontinuity in the \(E_a\) at \(~320\) K as well, but with larger values of 0.7 eV at low temperatures and 0.5 eV at high temperatures. While these studies agree that ion movement occurs in HOIPs, they disagree on the nature of the mobile ion and the mechanism of ion movement.

**1.4.3.4 Complications in Studying Ion Transport Under Illumination**

Many researchers have observed that ionic transport is enhanced under illumination.\(^\text{92, 96-98}\) However, performing many analytical techniques which could give information on this transport \textit{in-operando}, such NMR and SIMS studies, is non-trivial. The discrepancy in the ionic conductivity observed under dark and light has led some groups to question whether the nature of the mobile ion is the same under both conditions. Therefore, comprehensive studies need to be conducted in both light and dark
in order to gain a full perspective of ionic mobility. Unfortunately, introducing light to an experiment presents a logistical barrier for many analytical techniques and, as a result, many studies have been conducted only under dark.

Stability of HOIPs also needs to be considered when thinking about techniques to probe ion transport. Device stability has long been an issue for HOIPs and device degradation under certain conditions has been well documented in the literature. For instance, MAPbI$_3$ photovoltaic devices stored under dark in an N$_2$ environment have been reported to lose 20% of their original PCE over 24 hours. Conversely, devices stored in ambient air under dark lose nearly 80% of their efficiency over 24 hours.$^{99}$ When illuminated, devices degrade even more rapidly, losing 40% of their efficiency in an N$_2$ environment over 20 hours.$^{97}$ Strikingly, devices under illumination in dry air can degrade exceptionally fast; showing PCE depletion within minutes of exposure and rapidly declining to around 5% of their original PCE within 6 hours.$^{100}$ Though overall device stability relies on a multitude of factors including fabrication technique, device architecture, grain size, chemical composition, and temperature, HOIP devices are notoriously unstable to many device relevant conditions. The rapid degradation of HOIPs impacts the ability of researchers to conduct experiments that need to be taken over more than a few hours, especially in ambient air.

Time sensitivity is not the only stability-related difficulty when taking measurements; many techniques themselves have been shown to degrade devices more rapidly. EDX, x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, x-ray fluorescence (XRF), electron energy loss spectroscopy (EELS), and Rutherford backscattering (RBS) are all capable of inducing beam damage to HOIPs.$^{101}$ The
instability of HOIPs to beam damage limits the reliable data that can be obtained by using these techniques and must be considered when designing experiments. Degradation of the material during measurement can leave artifacts in the data and ultimately lead to inaccurate analysis. When selecting methods to study ion transport, therefore, it is imperative that a non-destructive technique that allows for illumination is used, preferably in a dry or anaerobic environment.

Electrochemical impedance spectroscopy (EIS) has recently emerged as a tool in HOIP literature to examine processes that occur at different time scales. The concept of “impedance” is analogous to resistance but allows for description of complex circuits which have non-linear current-voltage relationships, such as those which exhibit capacitance, inductance, or mass diffusion. EIS takes advantage of this concept by relating theoretical circuit elements to actual electrochemical processes occurring in a material and allowing fitting of current, voltage, and frequency data to equivalent circuit models. EIS data is generated by applying an AC potential to an electronic device, measuring the AC current response, and recording phase shift and amplitude changes over a range of applied frequencies. Examining the current response over a range of frequencies allows separation of processes which occur on different time scales, making it ideal for separating electronic and ionic processes in mixed conductors. This is a key advantage of EIS making it an apt tool to study ion diffusion in HOIPs and resolve the chemical identity of the ion.

EIS results are plotted by convention as a Nyquist plot, where the AC current response signal is separated into the real and imaginary components of impedance and plotted in complex space. The data closest to the origin is associated with the higher
frequency spectrum whereas the data farther from the origin is associated with the lower frequency spectrum. The analysis of data from impedance spectroscopy is not straightforward. As a first step, Nyquist plots of EIS data, with the real component of the impedance ($Z'$) on the horizontal axis, and the imaginary component ($Z''$) on the vertical axis, are fit with equivalent circuit models to quantitatively model device properties, as shown in Figure 10. The initial guesses for these models are based on knowledge of underlying physical processes in the system. The shape of the Nyquist plots also provides clues to the physical processes that may be involved. For example, if the Nyquist plot is a line parallel to the y-axis, then the equivalent circuit is composed of a capacitor in series with a resistor. The value of the resistance is the intercept on the x-axis. If the Nyquist plot is a semicircle and has an intercept at the origin, then the equivalent circuit is composed of a capacitor in parallel with the resistor. If there is a resistor in series to this circuit, then the semicircle is displaced on the x-axis and series resistance is the value of the displacement. Thus, visual examination of features of the Nyquist plot combined with knowledge or supposition of inner workings of the device allows for creation of an equivalent circuit model, where each circuit element represents a specific process. For example, a simple photovoltaic device which is only an electronic conductor can be modeled with just two elements, a resistor and a capacitor, where the resistor represents the resistance experienced by electronic charge carriers when moving through the active material and the capacitor represents the capacitance generated by differential separation of electrons and holes; this simple R-C circuit will appear as a semicircle in the high frequency region of the Nyquist plot (closer to the origin). Values for different circuit elements obtained upon fitting can give both qualitative ideas of how separate processes
in a device change with varying conditions as well as quantitative kinetic data such as time constants or activation energies for each separate process.

As mentioned before, HOIPs are semiconductors and ionic conductors. Thus, impedance plots contain information about both electronic and ionic processes. Often two distinct features are seen in the Nyquist plots of HOIP-based devices: a high-frequency semicircle and a low-frequency semicircle or linear feature (Figure 10). At high frequencies, electronic process typically dominates and devices can be modeled with a simple electronic RC circuit. At relatively low frequencies, ionic transport dominates, and the equivalent circuit model mirrors a Randles circuit model. Ionic transport does indeed dominate at low frequency and electronic dominates at higher frequency, but there are comparable ionic/electronic influences in the middle frequency ranges. However, these features change based on the device architecture and

**Figure 10:** Top: illustration of the form that basic circuit elements take on Nyquist plots. Bottom Left: basic schematic for reading Nyquist plots. Bottom Center and Right: Nyquist plots of a pure double layer capacitor vs a circuit which includes a linear Warburg diffusion element.
components. Hence, there is considerable debate about the physical process involved within a HOIP device.

Figure 11 shows equivalent circuit models tested for HOIP-based devices in the literature.\(^{105}\) Model A in this figure is the simplest circuit model, while Models B-D are slightly more complex. At high frequencies, Model B is a simple electronic RC circuit because the double-layer capacitance element is effectively shortened. At low frequencies, however, the circuit model mirrors a Randles circuit model because ionic transport dominated at low frequencies. Model C captures the coupled electronic/ionic transport, but the parallel resistor, \(R_{\text{elec}}\), is not coupled with ionic transport. Model D contains parallel electronic and ionic transport resistances, unlike the previous models. Model E replaces \(C_{\text{ion}}\) with a constant phase element (CPE), \(CPE_{\text{ion}}\), and shows an improved fit from Model C. In Models D and E, \(R_{\text{ion}}\) captures the resistance associated with lower frequency. Model E does couple electronic/ionic transport, unlike the resistor in Model C. Overall, Model F is used to create a robust equivalent circuit to fit a greater number of HOIP-containing samples. In model F - developed by Venkataraman and coworkers and used successfully by Fan and coworkers – electronic transport separated from ionic transport is modeled as a resistor (\(R_{\text{elec}}\)), and the ion diffusion is modeled with a special CPE known as a Warburg (\(W_s\)).\(^{94-95}\) The Warburg element captures mass transfer due to ion diffusion and appears as a diagonal line with the slope of 45° in the low-frequency part of the Nyquist plots.\(^{106-107}\) Mathematically, the impedance of a CPE is defined by the equation:

\[
Z(j\omega) = \frac{1}{Q(j\omega)^\alpha}
\]
where $Q$ is the CPE coefficient, $j = \sqrt{-1}$, $\omega$ is the angular frequency, and $\alpha$ is an exponent equal to 1 for an ideal capacitor. An ideal Warburg element has impedance:

$$Z_W(j\omega) = \frac{A_W}{\omega^\alpha} - \frac{jA_W}{\omega^\alpha}$$

where $A_W$ is Warburg resistance, and $\alpha$ is equal to 0.5. The Warburg element gives insight to diffusion based processes at high and low frequency ranges and is therefore an ideal element to consider when analyzing ion transport in the EIS spectra of HOIPs.
In order to accurately model EIS data for a device, each circuit element in the proposed model must correspond to a physical process. Figure 12 shows a schematic of
the corresponding physical processes in an HOIP PV device for the circuit model developed by Venkataraman and coworkers, including the accumulation region and the region of ion diffusion that extends into the bulk HOIP film. The equivalent circuit models that represent these EIS spectra combine both slow and fast charge transport processes. In this model, $R_{\text{el}}$ is not coupled with ionic transport. In the model developed by Venkataraman and coworkers, high frequency impedance data is modeled with bulk electronic charge transport/recombination resistance ($R_{\text{tr/rec}}$), and charge stored in the bulk of the HOIP active layer is modeled with a chemical capacitance element ($C_{\mu}$). The low frequency impedance data is modeled with a charge-transfer resistance ($R_{\text{CT}}$) and a double-layer capacitance ($C_{\text{DL}}$) to quantify changes in resistance and capacitance at the active layer/electrode barriers caused by ionic/electronic charge accumulation, as well as the Warburg element ($W_s$) to quantify ion diffusion through the HOIP active layer.

Figure 12: Schematic representation of the equivalent circuit model used in studies by Venkataraman and coworkers and Fan and coworkers. Additional resistance ($R_{\text{el}}$) is added in parallel for electronic transport which is not coupled with ionic transport.
Low frequency features in the EIS spectra of HOIP photovoltaics – corresponding to longer time scale processes – have been interpreted in many different ways in regard to ion transport. Initial studies of HOIPs which included electrochemical impedance analysis, such as by Grätzel and coworkers and Cameron and coworkers, observed irregularities in the low frequency regime of their EIS spectra but did not further analyze these features.\textsuperscript{112-113} Grätzel and coworkers later attempted to adapt an EIS circuit model developed for DSSCs to a solid state HOIP photovoltaic device.\textsuperscript{114} They noticed a feature in the low frequency regime that could appear alternately as a negative capacitance (inductance) or as an additional capacitive semicircle, and noted that it might be related to the reorganization of mobile ions at the interfaces. Interestingly, in moving from the DSSC circuit model to the solid state HOIP model, they removed a circuit element known as the Warburg diffusion element – which is typically used for modeling of ion diffusion in EIS experiments. They instead used a simple R-C circuit element that models ion accumulation at the ETL and HTL interfaces but does not account for mass transport through the film. Cahen and coworkers also observed a negative capacitance feature in the low frequency regime of their EIS spectra but rejected the hypothesis that it was related to ion/vacancy accumulation. They stated that this would only be the case if the ions/vacancies were able to affect the barrier for charge injection into the ETL/HTL and reasoned that this is not true for HOIPs.\textsuperscript{115} However, prior evidence has demonstrated that ion and vacancy accumulation is likely able to cause band bending at the ETL/HTL interfaces which would affect the barrier for charge injection; additionally, they noted that this low frequency feature disappears in samples measured in ambient air, which were speculated to be heavily n-doped. Cheng and coworkers did a seminal study by
performing EIS analysis on HOIP cells with varying architecture and doping levels. In their paper, they observe the signature of a Warburg diffusion element in their EIS spectra, mentioning that “the revealing 45° transport feature is observed in some cell architectures but not others.”\textsuperscript{116} None of their analysis, however, includes Warburg diffusion or attributes this low frequency response to ion transport. Instead, they ascribe the low frequency features to dielectric relaxation and view the relative doping only in terms of electronic charge carriers, despite prior evidence that ionic species can strongly influence doping levels.

While EIS has clearly uncovered a low frequency responsive feature in HOIPs which corresponds to a slow timescale process, analysis of this data and the circuit model which best describes it remains controversial. It is clear from the literature that the Warburg diffusion element recurs as a possibility without ever being seriously integrated into EIS analysis, despite mounting certainty that HOIPs are indeed capable of ion transport through the film. Venkataraman and coworkers incorporated the Warburg diffusion element in their analysis of the EIS spectra of MAPbI\textsubscript{3}, MA\textsubscript{x}FA\textsubscript{1-x}PbI\textsubscript{3}, and FAPbI\textsubscript{3}.\textsuperscript{94} They were able to use EIS to qualitatively identify that it corresponded to mass transport of the organic cation, providing evidence for its mobility, and quantify values for this ion such as diffusion coefficient and activation energy barriers. Fan and coworkers also observed the Warburg element in their EIS data and found evidence supporting the hypothesis that it arises from movement of the organic cation.
1.4.4 Improving HOIP Stability Under Light

Instability to light remains one of the biggest roadblocks to the realization of the many potential HOIP applications. There is still little consensus on how light interacts with HOIPs structurally, electronically, and chemically and how this leads to their degradation. Creation of electronic trap states under illumination has been proposed via a variety of mechanisms.\textsuperscript{117-118} Light-induced chemical reactions, either within the HOIP active material itself such as deprotonation or formation of methyl iodide, or with interfacial materials could lead to degradation.\textsuperscript{119-123} Halide anion and/or organic cation transport has been proposed to be activated by light.\textsuperscript{92, 124-127} Explanations of the effects of this ion migration on degradation are also varied, from creation of deep trap states at ionic vacancy sites or ionic double layers at interfaces to structural destabilization.\textsuperscript{73, 128-129} Some theories invoke multiple factors necessary for degradation to occur, such as heat plus light, water plus light, or oxygen plus light.\textsuperscript{100, 118, 124, 127, 130-131} HOIPs with the formamidinium (FA) cation substituted for MA in the A-site of the lattice show increased light stability across numerous studies.\textsuperscript{124, 132-134} However, there is similar debate about how FA increases stability. It is larger than MA, has a much smaller (near zero) dipole moment, and has two amine groups capable of hydrogen bonding as opposed to the single amine group present on MA. These factors affect the structure and electronics of mixed MA\textsubscript{x}FA\textsubscript{1-x}PbI\textsubscript{3} perovskites, and have also been proposed to slow or stop light-induced ion transport.\textsuperscript{129} Overall, there is a clear need for systematic studies investigating the complex interaction between light and HOIP materials.
2.1 Abstract

The field of organic photovoltaics (OPVs) has long focused on matching silicon solar cells, both in high power conversion efficiency (PCE) under solar light and broad absorption of the solar spectrum. We show that OPV devices, which have significantly lower PCEs than high-performing crystalline silicon cells when measured under the typical AM 1.5G solar standard, can surpass silicon cells with PCEs $>20\%$ measured under LED light. We highlight that the conflation of the terms ‘solar cell’ and ‘photovoltaic’ gives an incomplete view of the potential of many photovoltaic materials, especially organic materials. By expanding the definition and assessment of photovoltaic devices to include multiple light sources, OPVs—with their higher PCEs under indoor light and qualitative benefits of being lightweight, thin, flexible, and semi-transparent—could have a home in previously unconsidered low-power indoor applications.†

2.2 Introduction

The term ‘photovoltaic’ has become synonymous with the term ‘solar’ in both colloquial and professional usage. The AM 1.5G light that mimics the terrestrial solar spectrum is the standard illumination source for measuring power conversion efficiency

† This chapter was adapted with permission from Cutting, C.; Bag, M.; Venkataraman Indoor Light Recycling: A New Home for Organic Photovoltaics. J Mater Chem C 2016, 4, 10367–10370.
(PCE), which is the ratio of the electrical power output to the optical power input and is the decisive metric in this field. Thus, there is an implicit assumption that all photovoltaic devices will be used to convert solar energy to electrical energy. For example, the entry for solar cells in Wikipedia reads as “Solar cells are described as being photovoltaic irrespective of whether the source is sunlight or an artificial light”, while the entry for the term ‘Photovoltaics’ reads as “Photovoltaics (PV) is the name of a method of converting solar energy into direct current electricity using semiconducting materials that exhibit the photovoltaic effect.” This prevalent synonymy of the terms ‘photovoltaic’ and ‘solar’ has led to a myopic view of the possible applications of photovoltaic cells and the rejection of technologies that do not have PCEs measured using AM 1.5G comparable to crystalline silicon solar cells—the benchmark technology for high-efficiency commercial solar cells. This synonymy also leads to the common expectation that good solar cells will also be good photovoltaics i.e. devices with poor PCEs under AM 1.5G light source will also have poor PCEs under other light sources. Herein we show that common expectation is incorrect and the synonymy is a fallacy. We show that organic photovoltaics (OPVs), which have been viewed as subpar technology because their PCEs under the AM 1.5G light source have not yet matched crystalline silicon (c-Si) solar cells, can outperform commercial cells, including c-Si, under indoor light. We make the case that expanding the definition of a photovoltaic device to a device that converts photons into electrical energy will allow us to expand the discussion about harnessing light energy from the Sun and from other light sources such as indoor artificial light.
The performance of silicon solar cells with illumination sources other than AM 1.5G has been investigated because of the potential for energy generation under indoor lighting. Changing the light source from AM 1.5G to indoor lights not only changes the intensity but also the spectrum of the incident light. In c-Si cells, the PCE has a strong dependence on the light intensity but only a weak dependence on the light source. Thus, to simulate internal lighting, most studies use AM 1.5G light source with low intensities. The spectral irradiance of an AM 1.5G light source is broad and ranges from 400 nm to 2000 nm (Figure 13). Thus, for a solar cell to have high PCE, the active layer must have a broad absorption and have a good spectral match with the AM 1.5G light. Conjugated polymers, the active layers of OPVs, typically have poor absorption in the near infrared (NIR) region of the solar spectrum and do not have uniform absorption in the visible region (Figure 14). Thus they do not have a good spectral match with the AM 1.5G light and consequently have lower PCEs compared to silicon.
The last decade has witnessed a revolution in internal lighting with the phasing out of incandescent light bulbs and replacement with compact fluorescence lights (CFLs) and, more recently, with white light emitting diodes (LEDs).\textsuperscript{138, 147} Unlike incandescent light bulbs, which have broad emission spectra similar to AM 1.5G, CFLs and LEDs have narrow spectra primarily in the visible range (Figure 13). Under these light sources, newer technologies with better spectral match with white LEDs can outperform silicon (Figure 14). For example, it has been shown that dye-sensitized solar cells (DSSCs) have larger PCEs compared to silicon under CFL and LED illumination and that some OPVs show increased efficiency under CFL illumination.\textsuperscript{148-151} Herein we show that PCEs of greater than 20\% can be obtained in OPVs with white LED illumination, matching PCEs...
of polycrystalline silicon solar cells and surpassing amorphous silicon and copper indium gallium selenide (CIGS) solar cells.

Figure 14: Incident photon-to-electron conversion efficiency for the following devices: crystalline silicon (c-Si), amorphous silicon (a-Si), P3HT:PC60BM bulk heterojunction (P3HT:PC60BM BHJ), and PCE10:PC70BM bulk heterojunction (PCE10:PC70BM BHJ) devices. Also shown is the emission spectrum of a commercial white LED light. IPCE spectrum of CIGS is provided in Supplemental Figure 18 and IPCE spectrum of perovskite devices is provided in Supplemental Figure 19.

2.3 Experimental

For indoor light, we chose a commercial white LED bulb and the intensity 20.5 mW cm$^{-2}$. For outdoor light, we used an AM 1.5G solar simulator and the intensity 100 mW cm$^{-2}$. For a well-lit room, the intensity of the indoor light is approximately 0.5–1...
We obtained a representative selection of commercial photovoltaics with the materials which have the highest current market share: polycrystalline silicon (c-Si), amorphous silicon (a-Si), and copper indium gallium selenide (CIGS). We fabricated a representative selection of organic photovoltaic devices. We also fabricated inorganic–organic hybrid perovskite photovoltaics devices using a previously reported protocol. For amorphous silicon (a-Si) cells, we used a commercial cell in a toy (Dancing monkey doll, cell from Vimun SC-3012-2A-A17/5) and for polycrystalline silicon cells, we used an encapsulated commercial cell from a garden light (Malibu Lights). We used a CIGS device from Nanosolar Nanocell. Device performance (current density vs. voltage) under both the AM 1.5G solar simulator lamp and the commercial white LED light was tested in a glovebox (Figure 15). IPCE was measured in atmosphere from 400–1100 nm. See supplemental information for device fabrication and measurement details.

2.4 Results and Discussion

Under AM 1.5G illumination, the a-Si cell had a PCE of 1.45%, the CIGS cell had a PCE of 2.64%, and the c-Si cell had a PCE of 16.72%. For OPVs, we used devices with active layers P3HT:PC$_{60}$BM and PCE10:PC$_{70}$BM in bulk heterojunction (BHJ) morphologies. Under AM 1.5G illumination, the P3HT:PC$_{60}$BM device had a PCE of 2.93 ± 0.20% (7 devices) and PCE10:PC$_{70}$BM had a PCE of ± 0.4% (4 devices). We also used a device fabricated using aqueous dispersions of P3HT nanoparticles and PCBM nanoparticles, which had a PCE of 1.8 ± 0.04% (2 devices) under AM 1.5G illumination. MAPbI$_3$ and MA$_x$FA$_{1-x}$PbI$_3$ perovskite photovoltaics had PCEs of up to 12.49% and 8.80%, respectively, under AM 1.5G light, and showed PCEs of up to 33.22% and 22.18% under white LED illumination (Figure 15).
Figure 15: Comparison of PCEs of silicon, OPVs, and perovskite PVs under AM 1.5G solar simulator illumination (red) and under LED illumination (blue).

Under white LED illumination, both a-Si and c-Si showed only moderate increases in PCEs, consistent with earlier studies.\textsuperscript{154-155} a-Si had a PCE of 2.18\% and c-Si had a PCE of 20.19\%. CIGS showed a slight decrease in PCE down to 2.01\% under LED illumination because of its diminished absorption in the visible region (Supplemental Figure 18). However, OPVs show a dramatic increase in PCEs. The P3HT:PC\textsubscript{60}BM BHJ device showed a PCE of 12.83 ± 0.98\% and PCE10:PC\textsubscript{70}BM BHJ device showed a PCE
of 21.04 ± 2.08%. The P3HT:PC$_{60}$BM device fabricated from aqueous nanoparticle dispersions showed a PCE of 6.89 ± 0.46%.

The P3HT-based devices showed the largest increase in PCE (B300%) under LED compared to PCE under AM 1.5G whereas PCE of c-Si increased by 20%. We attribute the difference in percent increase in PCE to spectral overlap between the light source and the absorbance of the material, as shown by the external quantum efficiency (EQE) spectra overlaid with LED spectra (Figure 14).\textsuperscript{143-144} A great deal of organic photovoltaic research has been aimed at widening the absorbance profile of materials to capture more of the sun’s light, as evidenced by the higher wavelength and broader absorbance of PCE10, a newer OPV polymer,\textsuperscript{145-146} when compared with P3HT. While PCE10’s overall performance was higher, P3HT showed a much steeper increase in efficiency between solar and LED light because of good spectral match (Figure 16). We also observed a similar trend in P3HT:PC$_{60}$BM devices fabricated from aqueous nano- particle dispersions (Figure 16). These results may not be surprising in hindsight, but they quantitatively address and correct the common perception that poor solar cells will also be poor photovoltaics. Many organic materials previously dis- counted for use in photovoltaics due to an insufficiently broad absorbance spectrum could possibly be even more well-suited for indoor light than the materials tested here, finding a place inside our homes and offices.
Since the PCEs of the OPVs outperform silicon cells in internal LED lighting, they can also generate more power than currently used amorphous silicon cells. For example, a 10 cm x 10 cm OPV cell with a 10% PCE under 0.5–1 mW cm$^{-2}$ illumination (500–1000 lux) will generate 5–10 mW whereas a-Si cell with comparable dimensions will generate only 1–2 mW. Thus OPVs can conveniently replace a-Si cells in many applications such as calculators, clocks, scales, or novelty items (Figure 17).\textsuperscript{156} Others applications such as wearable electronics,\textsuperscript{157-160} detectors, sensors, remote control
equipment, wireless computer mice and key-boards, flashlights, radios, and automatic paper towel, soap, and hand sanitizer dispensers may be powered by OPV-charged batteries, thus extending the time required for re-charging.\textsuperscript{140} Photovoltaic panels could be incorporated directly into these types of devices, or simply be installed as panels on walls, floors, or other surfaces to power nearby devices or put electricity back into the building power supply (Figure 17). Additionally, the qualitative advantage of OPVs over c-Si cells of being thin, semi-transparent, and flexible allows them to be used on a number of surfaces which would be otherwise impossible, such as being put on curved surfaces like lampshades or flexible surfaces like blinds or curtains.

\textbf{Figure 17:} (left) A future house with OPV thermostat, computer mouse, remote control, curtains, lampshades and coffee table mats for re-using indoor light; and (right) power requirements for various devices used indoors and power from a 1 cm\textsuperscript{2} OPV cell.\textsuperscript{150}

There are numerous advantages of using photovoltaics to power indoor devices and wearable electronics.\textsuperscript{141, 157-160} Many indoor environments, like offices and some homes, are lit for the majority of the day. Intensities of indoor light range from 100 lux in homes and lightly used office spaces, to 500 lux for more heavily used office spaces, up to 1000 lux for spaces like warehouses or manufacturing lines.\textsuperscript{141, 151} Light intensities in
this range are sufficient to supply mW power with a few cm scale devices with PCEs observed under white LEDs in our OPV samples. These photons, which are otherwise effectively wasted, can be recycled to reduce the power demands of the building in which they are installed. Additionally, using photovoltaics for low power devices instead of the power grid or running solely off battery power translates to a reduction of need for copper wire and battery waste, as well as increasing the time between battery replacements.

2.5 Conclusions

In summary, we have demonstrated that OPVs can have higher PCEs than CIGS and Si-based solar cells under indoor LED lighting. Thus, several organic photovoltaic materials that had been previously discounted because of their low PCEs under AM 1.5G solar simulator light may have competitive efficiencies under indoor lighting. The better performance of OPVs under white LEDs coupled with their lightweight, flexible, and semi-transparent properties opens a wider variety of indoor applications, which had not been possible before with silicon cells. Our work only scrapes the surface of the hundreds of organic photovoltaic materials that have been developed and subsequently discounted for outdoor applications that may be ideal for these types of indoor light recycling applications. The need of the hour is to develop new standard conditions to evaluate PV devices under indoor lighting conditions.\textsuperscript{138, 154} Silicon may dominate the solar market for larger power applications in the near future but, as our work shows, may not be the ideal material for low power applications. The fact that OPVs can outperform silicon cells in indoor lighting opens a new and untapped avenue for energy harvesting applications.
2.6 Supplemental Information

Devices were fabricated on indium tin oxide (ITO) coated glass substrates with resistance of ~60 Ω. Substrates were cleaned by sonicating 20 min each in DI water with Fisher VersaClean soap, DI water, acetone, and isopropanol, then drying at least 2 hours in 140 ºC oven and storing in oven until ready to use. Heraeus Clevios PVP 4083 PEDOT:PSS hole transporting layer (HTL) was spin coated onto the substrates at 2500 rpm for 40 s, annealed in 140 ºC oven for 30 min, then removed and kept at room temperature for no more than 24 h before spin coating active layer.

P3HT:PC₆₀BM bulk heterojunction (BHJ) active layer was spin coated in air from a 20 mg/mL 1:0.8 molar ratio solution in chlorobenzene at 1000-1200 rpm for 60 s with 1.0 s ramp, then annealed at 150 ºC for 10 min in a glovebox.

P3HT:PC₆₀BM nanoparticle (NP) solution consisted of 1:1 ratio of separate P3HT and PC₆₀BM nanoparticles (~80±20 nm diameter) stabilized by sodium dodecyl sulfate in water. This solution was spin coated at 1100 rpm for 10 s with a 0.5 s ramp, then 1400 rpm for 20 s with a 0.5 s ramp, then 2000 rpm for 10 s. 15 mg/mL PC₆₀CM solution in DCM was then spin coated on top at 1000 rpm for 30 s, then 2000 rpm for 10 s.

PCE10:PC₇₀BM BHJ active layer was spin coated in a glovebox from a 1:1.8 weight ratio solution in chlorobenzene:1,8-diiodooctane (3 v% DIO) which was stirred at 55 ºC for 1 day. DIO was removed under vacuum. 15 nm of C₆₀-N was spin-coated on top.

MAPbI₃ and MA₀.₅FA₀.₅PbI₃ devices were fabricated by spin coating 400 mg/mL PbI₂ solution in DMF at 6000 rpm for 35 s, followed by annealing at 75-80 ºC for 45 min. On top of this was spin coated a 40 mg/mL solution of either MAI or 1:1 MAI:FAI
at 6000 rpm for 35 s, followed by annealing at 75-80 °C for 45 min. 20 mg/mL PC$_{60}$BM solution in chlorobenzene was then spin coated on top at 1000 rpm for 60 s, then 2000 rpm for 10 s.

15 nm of Ca followed by 100 nm of Al as cathode electrode was thermally deposited at 10$^{-6}$ mbar pressure on top of the active layer of MAPbI$_3$, MA$_{0.5}$FA$_{0.5}$PbI$_3$, and P3HT:PC$_{60}$BM BHJ and NP devices. 100 nm of Ag was thermally deposited at 10$^{-6}$ mbar pressure on top of the active layer of PCE10:PC$_{70}$BM BHJ devices. All devices fabricated in house had active area of 6 mm$^2$ and 4 devices per substrate.

Figure 18: Incident photon-to-electron conversion efficiency for Nanosolar Nanocell copper indium gallium selenide (CIGS) photovoltaic cell. Also shown are the emission spectra of an AM1.5G solar simulator and a commercial white LED light.
Figure 19: Incident photon-to-electron conversion efficiency of MAPbI$_3$ and MA$_{0.5}$FA$_{0.5}$PbI$_3$ perovskite PV devices. Also shown is the emission spectra of a commercial white LED light.
CHAPTER 3

ORIGIN OF LOW OPEN CIRCUIT VOLTAGE IN SURFACTANT-STABILIZED ORGANIC NANOPARTICLE-BASED SOLAR CELLS

3.1 Abstract

Organic nanoparticle-based solar cells have drawn great attention due to their environmentally friendly fabrication procedure. However, these surfactant-stabilized nanoparticles suffer open circuit voltage losses due to charge trapping and poor extraction rate at the polymer cathode interface. Here we have investigated the origin of voltage loss and charge trapping in surfactant-stabilized nanoparticle-based devices. Efficient organic photovoltaic (OPV) devices have been fabricated from an aqueous dispersion of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) nanoparticles stabilized by anionic surfactants. AC impedance spectroscopy has been used to understand the charge transport properties in the dark and in operando conditions. We have demonstrated the similarities in the charge transport properties as well as photocarrier dynamics of the nanoparticle-based OPVs and the bulk hetero-junction OPVs despite fundamental differences in their nanostructure morphology. This study emphasizes the possibility of fabricating highly efficient OPVs from organic nanoparticles by reducing surface defects and excess doping of the polymers.‡

‡ This chapter was adapted with permission from a manuscript submitted to ACS Applied Materials and Interfaces in 2019 authored by Timothy S. Gehan, Christie L.C. Ellis, Dhandapani Venkataraman, and Monojit Bag.
3.2 Introduction

Organic nanoparticle-based devices are the emerging technology for next-generation optoelectronic applications, especially in the field of organic solar cells. Organic nanoparticle-based device processing overcomes the two major roadblocks for current state-of-the-art organic photovoltaic technology through its use of an environmentally benign aqueous solvent to replace the toxic haloarene solvents previously used for large scale printing on flexible substrates and its tunable morphology of the active layer materials at multiple length-scales. Organic nanoparticles are generally synthesized by the miinium emulsion method. These nanoparticles are stabilized by ionic or neutral surfactants. The common expectation was that the surfactant molecules would impede the charge transport as observed in inorganic nanoparticles assemblies. However, it was previously shown that if excess surfactants were removed from the nanoparticle dispersion, then the charge transport properties of these nanoparticles assemblies are comparable to that of the pristine polymer. Recent reports have shown that stripping excess surfactant to improve device stability as well as efficiency can minimize the formation of microstructural defects. So far, efficiencies have reached over 7.5% for low band gap polymer/non-fullerene acceptor nanoparticle-based solar cells. There are multiple length-scales at which electron-donating as well as electron-accepting polymers or molecules need to be assembled to achieve maximum efficiency in organic solar cells. Tunable aggregate structure within the nanoparticles along with the random assembly of binary polymer nanoparticles, both of which are necessary for efficient devices, have been demonstrated previously. The major concern is still whether these surfactant-stabilized nanoparticle-based devices
could outperform the bulk heterojunction organic photovoltaic (BHJ-OPV) cells prepared from organic solvents. In this work, the efficiency of surfactant-stabilized poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) nanoparticle-based organic photovoltaic (NP-OPV) cells has reached over 2%. We have demonstrated that these NP-OPVs do have high fill factors (FF) over 66% as well as high current densities ($J_{sc}$). However, achieving high open-circuit voltage ($V_{oc}$) is still elusive in these NP-OPVs, leaving opportunities for further improvement. There are reports of NP-OPVs fabricated from low molecular weight P3HT polymer ($M_w \sim 12$ kDa) with high $V_{oc}$, but the overall power conversion efficiency (PCE) is very low. Gärtner et. al. has demonstrated a polymer nanoparticle device fabricated using a surfactant free re-precipitation method which has both comparable $V_{oc}$ and power conversion efficiency as reported in BHJ-OPVs. There have been very few reports on the charge transport properties especially in surfactant-stabilized organic nanoparticle-based solar cells. Recently, Colberts et. al. demonstrated that surfactant impacts the device performance which was limited by bimolecular recombination loss. Ameri et. al. have shown that free surfactant can influence charge and ion transport in organic nanoparticle-based optoelectronic devices by creating a large capacitance. However, they concluded that the electronic density of trap states and charge carrier mobility do not depend on the unbound surfactant, although the surfactants can diffuse towards the electrode interface and hinder the charge extraction. Subianto et. al. used a sulfonated thiophene derivative to control the morphology of the polymer/fullerene blend nanoparticles, which significantly impacted the photocarrier generation and charge transport in these nanoparticles by homogeneously de-mixing P3HT and PCBM small domains.
Therefore, there is a need to understand the basic working mechanism of these nanoparticle-based photovoltaic devices and find out if there is any fundamental difference between NP-OPVs and BHJ-OPVs in order to increase the power conversion efficiencies of NP-OPVs to a level competitive with BHJ-OPVs. In this article, we have addressed some of the major concerns related to the working principles of NP-OPVs and directly compared them with the BHJ-OPV device parameters to identify the origin of low $V_{OC}$ of these NP-OPVs using impedance spectroscopy (IS), which has been previously used to understand BHJ-OPVs.$^{175-178}$

### 3.3 Materials and Methods

#### 3.3.1 Device Fabrication

BHJ-OPV devices of P3HT and PCBM (1:1 by wt. ratio) were fabricated in air from chlorobenzene (20 mg mL$^{-1}$ concentration) to best compare with NP-OPV devices fabricated outside glove box from separate nanoparticles ($\sim$80 ± 20 nm diameter) of P3HT and PCBM (1:1 number ratio).$^{14}$ Details of P3HT and PCBM separate nanoparticle synthesis and characterization is given in supporting information (Supplemental Figure 25, Figure 26, and Figure 27). Photovoltaic devices were prepared using a thin coating of PEDOT:PSS as a hole transporting layer (HTL), between active materials and indium tin oxide (ITO) coated glass substrate, to facilitate ‘hole’ carrier extraction from the active layer by creating an ohmic contact with the polymer interface. PCBM (20 mg mL$^{-1}$ concentration in dichloromethane) was spin-coated on top of the organic nanoparticle active layer before cathode deposition, as hole blocking layer at the cathode interface. Finally, a thin layer (15 nm) of Ca followed by a thick layer (100 nm) of Al were
thermally deposited as the cathode on top of the active layer of both BHJ-OPV as well as NP-OPV devices.

### 3.3.2 Dark and Light J-V Device Measurement

The current density-voltage (J-V) characteristics were measured inside a nitrogen-filled glove box in the dark as well as under an AM1.5G solar simulator at 100 mW cm\(^{-2}\) light intensity. The maximum PCE for NP-OPVs fabricated from separate nanoparticles of P3HT and PCBM was 2.2%, with \(J_{sc} \sim 7.2\) mAcm\(^{-2}\), \(V_{oc} \sim 0.49\) V and FF over 62% (Supplemental Figure 28). Considering the statistical variation in \(V_{oc}\), \(J_{sc}\) or PCE (Supplemental Figure 29), we have used average efficiency (PCE \(\sim 1.9\%\)) NP-OPV device with lower \(V_{oc}\) but with higher \(J_{sc}\) to match with BHJ-OPV devices to understand the importance of various device parameters. J-V characteristics of BHJ-OPV and NP-OPV device are shown in Figure 20(a). There is not much difference in \(J_{sc}\) (\(\sim 8\) mA cm\(^{-2}\)) and fill factor (55 - 60%) for these two device architectures. The main difference in device performance is attributed to a significant drop in \(V_{oc}\) for NP-OPV devices (\(\sim 0.44\) V) compared to BHJ-OPV devices (\(V_{oc} \sim 0.57\) V). The dark current densities from these two devices are plotted in Figure 20(b). NP-OPV devices shows higher dark current density compared to BHJ-OPV devices. The ‘hole’ carrier mobility of the NP-OPV device (5.2×10\(^{-4}\) cm2V\(^{-1}\)s\(^{-1}\)) calculated from the space charge limited current (SCLC) measurement (Supplemental Figure 30) is unexpectedly higher than the ‘hole’ mobility calculated for BHJ-OPV device (3.8×10\(^{-4}\) cm\(^2\) V\(^{-1}\)s\(^{-1}\)). In both cases active layer thickness measured by Alpha step IQ profilometer was around 120 – 130 nm.
Figure 20: (a) Device J-V curve for BHJ-OPV and NP-OPV under 100 mWcm$^{-2}$ light intensity. (b) Dark J-V characteristics of the two samples. Inset: Dark J-V in linear scale.

3.3.3 Mott-Schottky Measurement

To understand the polymer/cathode interfacial properties and the band structure (flat band potential $V_{fb}$), a capacitance-voltage (C-V) measurement was carried out at 10 kHz frequency in the dark as well as under AM1.5G solar simulator at 100 mWcm$^{-2}$ light intensity. The capacitance measurement of the BHJ-OPV and the NP-OPV is shown in Figure 21(a). The corresponding Mott-Schottky plot of the NP-OPV and BHJ-OPV devices under dark is shown in Figure 21(b), and Mott-Schottky plot under photo-
illumination is shown in Figure 21(c). Four distinct regimes can be seen in the C-V plot:

1. At high reverse applied voltage ($V_{app} << V_{fb}$), polymer films behave like a dielectric. The depletion layer extends to the film thickness. The capacitance is very low and is determined by the geometrical capacitance value $C_g$;
2. At a voltage $V_{app} < V_{fb}$, capacitance increases due to depletion layer modulation;
3. At a voltage $V_{app} > V_{fb}$, depletion zone collapses and the overall capacitance is governed by the chemical capacitance $C_\mu$ (the storage of excess charge carriers);
4. At very high forward bias $V_{app} >> V_{fb}$, capacitance starts to drop due to minority carrier storage and eventually saturates at a lower value.

Figure 21: Capacitance Voltage (C-V) measurement of BHJ-OPV and NP-OPV device under (a) dark and illumination. (b) MS plot of two samples under dark and (c) under 100 mWcm$^{-2}$ light intensity.
The origin of $V_f$ in these photovoltaic devices is given by $V_f = \Phi_s - \Phi_c$, where $\Phi_s = E_{F0}$ is the Fermi level of the polymer blend and $\Phi_c$ is the cathode electrode work function as shown in Figure 22(a). It is expected that the $V_f$ under dark condition (also known as built-in field $V_{bi}$) should be as high as $V_{oc}$ (Supplemental Figure 31). However trapped charges at the interface may reduce the $V_f$ from the expected value (Figure 22(b) & (e)). $V_f$ is measured to be ~0.38 V for both BHJ-OPV and NP-OPV due to charge carrier (hole) accumulation at the cathode interface when the polymer/cathode interface was established. The carrier density at the polymer/cathode interface is estimated from Mott-Schottky plot, indicating high dark carrier (hole) concentration ($N_D = 3.3 \times 10^{16}$ cm$^{-3}$) in NP-OPV compared to that of BHJ-OPV ($N_D = 1.7 \times 10^{16}$ cm$^{-3}$). High dark carrier concentration could be also responsible for high charge mobility in NP-OPV devices. Under photo-illumination, $V_f$ is reduced due to the splitting of quasi-Fermi level of electrons and holes at respective interface (Figure 22(c) & (f)). In the case of BHJ-OPV, $V_f = -50$ mV when illuminated due to minority carrier (electron) accumulation at the interface, whereas NP-OPV shows $V_f = 80$ mV after illumination. In NP-OPVs, significant band bending occurs due to trapped holes near the cathode electrode, as shown in Figure 22(f). These trapped carriers reduce the quasi-Fermi level of the free electrons at the cathode interface. As a consequence, the $V_{oc} (= E_{F_n} - E_{F_p})$ of these NP-OPV devices decreases. Interestingly the difference in flat band potential in NP-OPV and BHJ-OPV under illumination is 0.13 V (see in Figure 22(c)), which is equal to the difference in $V_{oc}$ of these two devices. A control experiment was carried out on BHJ-OPV device with a thin layer of surfactant spin coated on top of the polymer film prior to cathode
deposition to understand the impact of surface defect states. A drop of ~50 mV in $V_{OC}$ (= 0.52 V) compared to reference cell is observed due to charge trapping at the cathode interface. The overall efficiency ($\eta$~1.6%) decreases significantly due to poor charge extraction at the cathode interface, however bulk charge mobility remains the same (Supplemental Figure 32).

Figure 22: (a) A schematic band diagram of BHJ-OPV before contact formation (before equilibrium), (b) after contact formation (after equilibrium) in dark, and (c) after contact formation under illumination. (d) A schematic band diagram of NP-OPV before contact formation, (e) after contact formation in dark, and (f) after contact formation under illumination. The empty circles represent trapped holes near cathode interface. $E_{F0}$, $E_{Fn}$, and $E_{Fp}$ are the Fermi energy of semiconductor blend, quasi-Fermi level for electrons, and quasi-Fermi level of holes, respectively.

### 3.4 Results and Discussion

#### 3.4.1 Analysis of Impedance Data

To understand the working principles of NP-OPVs and compare with the state-of-the-art BHJ-OPVs, we have carried out AC impedance spectroscopy (IS) analysis of the two samples. The devices can be analyzed using an equivalent circuit based on the series resistance ($R_s$), followed by a transmission line (TL) and Gerischer model\textsuperscript{179-180} for
organic solar cells consisting of transport resistance ($R_{tr}$), chemical capacitance ($C_{\mu}$) and recombination resistance ($R_{rec}$) and/or Gerischer impedance ($R_G$). We have also taken into account the interfacial or contact resistance ($R_{co}$) and capacitance ($C_{co}$) to analyze the high-frequency response. The impedance plot of two samples at different bias voltages is shown in Figure 23. $R_s$, $R_{co}$ and $C_{co}$ values are not listed here because of their minor differences at the high-frequency response originating from the polymer/electrode interface. The major difference in these devices arises from the recombination arc at different bias voltages. At low bias voltages, $R_{tr} < R_{rec}$ and hence the recombination arc is determined by the $R_{rec}C_{\mu}$ time constant (electron lifetime $\tau_n$). At low applied voltage, carrier diffusion length ($L_n$) for BHJ-OPV is more than the thickness of the film ($L$), as shown in Figure 23(a). Three parameters then can be extracted from the impedance plot from a TL model: $R_{tr}$, from Warburg impedance of diffusion at high frequency turning into a semicircle at low frequency, and $C_{\mu}$ and $R_{rec}$ from the recombination arc. The estimated diffusion length of the carrier at a bias voltage of 200 mV is $L_n = 1.35L$, as shown in Figure 23(a). In the case of NP-OPV, carrier diffusion length $L_n < L$ even at low field regime as observed from the impedance plot shown in Figure 23(b). Therefore, $R_{tr}$ or $R_{rec}$ cannot be extracted separately from the impedance plot. The overall capacitance $C_{\mu tot}$ and Gerischer resistance ($R_G$) is estimated from $\tau_n=R_GC_{\mu tot}$. At an applied voltage close to or higher than $V_{OC}$, $R_{rec} < R_{tr}$, and hence both BHJ-OPV and NP-OPV devices, follow the Gerischer impedance model. The recombination arc is then governed by the $R_GC_{\mu tot}$ relaxation time.). Interestingly, at $V_{OC}$, impedance spectra of both the devices overlap, as shown in Figure 23(c), indicating similar transport properties and relaxation mechanism present in these devices. However, devices with different $J_{SC}$ may
show slightly higher or lower $R_G$ at $V_{OC}$ (Supplemental Figure 35, Figure 36, and Figure 37).

**Figure 23:** (a) Nyquist plot of BHJ-OPV under 100 mWcm$^{-2}$ illumination at 200 mV DC bias, (b) Nyquist plot of NP-OPV under illumination at 100 mV DC bias. (c) Nyquist plot of two samples under illumination at DC bias voltages equal to the respective device $V_{OC}$. (d) Equivalent transmission line model of OPVs.

### 3.4.2 Origin of Capacitance

The total capacitance of these devices partly arises from the charge trapping and de-trapping phenomenon especially at low frequency regime.$^{181-182}$ First, if we assume a single trap state with a single relaxation time, the capacitance at low frequency is given by $C_\mu = C_0 + C_{trap}$ and the trapping kinetics provide the characteristic frequency $\omega t/2\pi$. Above this, frequency contribution from $C_{trap}$ tends to zero, and $C_\mu$ should be given by $C_0$. However, our experimental data of BHJ-OPV and NP-OPV at low bias voltages does not follow the single Debye relaxation model (Supplemental Figure 38). To best fit the experimental data, we have considered a multi-trap model with a power-law relaxation of the chemical capacitance $C_\mu \propto (i\omega)^{-\alpha}$ at frequencies higher than the characteristic
frequency $\omega t$. It is a phenomenological model of capacitance known as a constant phase element (CPE), which has two components: a constant value CPE-T and a power factor CPE-P where $0 \leq CPE-P \leq 1$, especially in the low voltage regime ($V_{app} < V_{OC}$). Fit parameters are listed in Table S1 in Supplementary Information at a bias voltage $V_{app} = 100$ mV, 400 mV and $V_{OC}$. CPE-P indicates the dispersive nature of the carrier lifetime. Incidentally, at $V_{app} = V_{OC}$, CPE-P = 1 for both the devices, indicating a low de-trapping rate. This could be due to higher charge recombination at open circuit conditions.

### 3.4.3 Effect of DC Bias Voltage

We have carried out bias dependent IS measurement of BHJ-OPV and NP-OPV to understand the transport behavior at different voltage regime. At low applied bias the free carrier lifetime is dominated by trapping de-trapping rate and the lifetime is of the order of few ms (Figure 24). As the applied voltage increases and it approaches towards $V_{OC}$, carrier lifetime decreases sharply till 0.35 to 0.5 V for NP-OPV and BHJ-OPV respectively. Near $V_{OC}$ the photogenerated carriers goes under bimolecular recombination loss which gives rise to shorter lifetime of the order of few $\mu$s. As the applied voltage increases beyond $Voc$ the lifetime starts to increase again as it is dominated by the charge transport phenomenon. Therefore, an anomalous behavior is observed in the measurement of free carrier lifetime which goes to minimum just before the applied voltage is equal to $Voc$. Under illumination, the carrier lifetime in BHJ-OPV and NP-OPV devices become comparable at low field regime but deviates as they approach $V_{OC}$. But both the lifetime become equal at their respective $V_{OC}$. In this study we have observed that the difference in voltage at which both the devices have shorter lifetime is order of 0.13 V. We have calculated recombination ($R_{rec}$) or Gerischer resistance ($R_G$) for
these two devices gives a clear indication that there is a minimum around $V_{OC}$ of the respective devices. The measured capacitance however increases with the applied voltages approaching $V_{OC}$ (Supplemental Figure 39). Beyond that voltage capacitance decreases again. We have also carried out intensity-dependent impedance measurement for both BHJ-OPV and NP-OPV. The carrier lifetime ($\tau_n$) is calculated from the Nyquist plot at 0 V applied bias as well as 200 mV applied bias (Supplemental Figure 40). There is not much of difference observed between BHJ-OPV and NP-OPV in terms of carrier lifetimes as they both follow bimolecular recombination mechanism.

![Figure 24: (a) Carrier lifetime estimated from the impedance plot at different bias voltage under dark condition. (b) Carrier lifetime under illumination at 100 mW cm$^{-2}$.](image)

**3.5 Conclusions**

In conclusion, low open-circuit voltage due to defect states at the interface and excessive doping of the polymer increases the dark carrier concentration during nanoparticle synthesis limits the efficiency of the organic nanoparticle-based solar cells. Reducing the dark carrier concentration by de-doping the polymer nanoparticles or avoiding exposure to oxygen during nanoparticle synthesis could both lead to more efficient NP-OPV devices. The effective carrier diffusion length is smaller in
nanoparticle-based devices compared to bulk hetero-junction devices. However, carrier lifetime, recombination rate, and transport properties in the bulk of the nanoparticle assembly and the bulk hetero-junction solar cell are observed to be same at open circuit condition. Further optimization is thus needed to reduce the potential energy loss due to deep trap sites at the interface and increase overall power conversion efficiency by improving the open circuit voltage.

3.6 Supplemental Information

3.6.1 Materials Used

P3HT was bought from Rieke Metals Inc. with Mw = 36 kDa, regioregularity = 96%, D = 2.3. PC$_{61}$BM was purchased from Nano-C. Dodecylsulfate Sodium Salt (SDS) with 98% purity was used. Conductive polymer PEDOT:PSS (Clevios P VP AI 4083) was used as received from Heraeus, conductivity 0.2 to 2 mS/cm. Commercial ITO substrates from Thin Film Devices Inc of 20 ± 2 ohm/sq sheet resistivity were used for all the measurements. Optical transparency was 88% at 550 nm.

3.6.2 Nanoparticle Dispersion Preparation

In a typical synthesis of P3HT:PCBM blend NPs, P3HT and PCBM were combined (1:1 by weight ratio) and dissolved in chloroform to form a 30 mg/mL (total) solution. This solution was heated and stirred for 30 min at 35°C to ensure dissolution. Then, aqueous 10 mM sodium dodecylsulfate (SDS) solutions were prepared using nanopure water, then warmed and sonicated with a VWR Aquasonic bath sonicator to ensure complete dissolution. Next, 3.0 mL of SDS solution was added to a 15 mL centrifuge tube, followed by 0.5 mL of the 30 mg/mL P3HT:PCBM blend solution. The resulting solution was immediately ultrasonicated in the centrifuge tube while cooling.
with an ice bath, using a MISONIX probe ultrasonicator for 2 min at 20% maximum amplitude with a 1/8” probe tip. During ultrasonication, the tip of the probe was placed just below the point where the centrifuge tube tapered, making sure that the probe was not touching the sides of the tube. After ultrasonication, the emulsion was poured into a glass vial and heated at 70°C for 40 min with constant stirring. This process is repeated for a second blend NP solution.

To remove excess surfactant from the NP solution, both blend NP solutions were placed in Vivaspin 6 centrifugal concentrator tubes (10 kDa molecular weight cut-off (MWCO)) and centrifuged at 4185 relative centrifugal force (rcf) for 25 min. The retentate volume was raised to approximately 5 mL with nanopure water and the samples were gently mixed and centrifuged again. This was done four times. In a fifth and final centrifugation cycle, the retentate volume was raised to 5 mL with a 20 vol% ethanol in water solution. This solution was centrifuged for 38 min at 4185 rcf. The retentate volume was raised to 0.5 mL with 20 vol% ethanol in water solution. This concentrated solution is then used for spin coating.

For the separate NP solutions, two NP solutions are prepared: one starting from 30 mg/mL of P3HT in chloroform and the other starting from 30 mg/mL of PCBM in chloroform. Both solutions are combined into a 6 mL centrifugal concentrator tube (10 kDa MWCO), following which the same centrifugal filtration process described above is performed.

3.6.3 Device Fabrication

ITO substrates were cleaned by ultrasonication in soap solution, rinsed several times with distilled water, then subjected to ultrasonication in acetone, then in isopropyl
alcohol. Substrates were then kept in hot-air oven at 90 °C for about 3 hours. Cleaned ITO substrates were treated with UV-O₃ (UVO Cleaner, Model 342, Jelight Company, Inc.) for about 15 minutes. Next, a 40 nm thick layer of PEDOT:PSS was spin-coated at 2500 rpm for 40 s (G3P-8 Spin Coater, SCS) after filtering through a 0.45 μm PTFE filter (Wilkem Scientific) under ambient conditions. PEDOT:PSS coated substrates were then annealed at 150°C for 30 min in air and allowed to cool to room temperature. The resulting substrates were then treated in the UV-O₃ for 3 minutes. An aqueous NP dispersion was then spin coated onto the PEDOT:PSS coated ITO substrates at 1000 rpm for 50 s in presence of an infra-red (IR) lamp. NP-coated substrates were then kept in a vacuum chamber for 12 h at 10⁻² mbar pressure. A PC₆₁BM buffer layer was spin coated inside a glove box onto the active layer at 1000 rpm, using a 15 mg/mL concentration in dichloromethane solution. The device was then transferred to electrode deposition chamber at 1×10⁻⁶ mbar, and a 15 nm layer of Ca was vapor deposited using a shadow mask of 6 mm² area at 0.5 Å/s deposition rate, followed by a 100 nm layer of Al deposited at a 1-3 Å/s deposition rate. The final devices were then annealed slowly from 30 °C to 150 °C inside the glove box. Device performance was tested under AM 1.5G solar simulator at 100 mW/cm² light intensity without using any physical/photo mask: the active area of the devices was calculated based on the Ca/Al deposition area. Reference cells were prepared by spin coating of P3HT:PCBM (1:1 by weight ratio) from chlorobenzene (20 mg ml⁻¹) solution at 1000 rpm for 60 seconds inside N₂-filled glove box, followed by annealing at 120 °C for 10 min. Ca/Al was thermally deposited as discussed before.
AC impedance is measured inside the glove box to avoid electrode degradation using Agilent 490A. Device impedance was measured under dark conditions and under illumination at 100 mWcm$^{-2}$ light intensity with variable DC bias voltages. AC amplitude was kept constant at 20 mV and the frequency ($\omega$) was swept from 100 Hz to 1 MHz.

3.6.4 Supplemental Figures

Figure 25: Nanoparticle Tracking Analysis to measure particle size. Particle size distribution of a P3HT and PCBM blend (1:1) NPs synthesized from various concentrations of active layer material (mg/mL) with various concentrations of surfactant (mM SDS).
Figure 26: UV-VIS absorption spectrum (a) P3HT and PCBM blend (1:1) NPs synthesized from 3 different concentrations of polymer in chloroform and added to 10 mM SDS surfactant. Corresponding NPs sizes are 70 nm, 80 nm, and 90 nm. b. P3HT and PCBM separate NPs synthesized from 15 mg/mL, 30 mg/mL, and 60 mg/mL concentrations of polymer in chloroform and added to 10 mM SDS surfactant. In case of separate NP dispersions, increasing crystallinity due to increase in NP size is observed (black arrow).
Figure 27: SEM image of P3HT and PCBM blend NP sample spin coated on PEDOT:PSS coated Si substrate.
Figure 28: $J$-$V$ curve of Blend and Separate NP-OPV under 100 mWcm$^{-2}$ light intensity.
Figure 29: $J$-$V$ curve of Separate NP-OPV under 100 mWcm$^{-2}$ light intensity. Four different set of devices showing variation in $V_{OC}$, $J_{SC}$, $FF$ and efficiency.
Figure 30: Current-voltage measurement under dark condition. Four distinct regimes are highlighted in color: (I) ohmic current (II) trap-limited space charge current (III) charge injection limited current and (IV) trap free space charge current.
Figure 31: (a) Light and dark C-V measurement of BHJ-OPV device with \( V_{oc} = 0.569 \) V, \( J_{sc} = 7.98 \) mA/cm\(^2\) and \( \eta = 2.69 \) % efficiency (b) light and dark C-V measurement of NP-OPV device with \( V_{oc} = 0.453 \) V, \( J_{sc} = 6.49 \) mA/cm\(^2\) and \( \eta = 1.68 \) % efficient device (c) M-S plot of BHJ-OPV device with carrier density at the interface estimated from the slope of the M-S plot (1.7 \( \times 10^{16} \) /cm\(^3\) in dark and 3.8 \( \times 10^{16} \) /cm\(^3\) in light) (d) M-S plot of NP-OPV device with estimated carrier density at the interface (2.6 \( \times 10^{16} \) /cm\(^3\) in dark and 4.9 \( \times 10^{16} \) /cm\(^3\) in light).
Figure 32: BHJ-OPV with SDS layer (a) current-voltage measurement under dark condition in semi-log scale. (b) $J-V$ curve under illumination as well as under dark (c) IS plot at different dc bias voltage (d) IS plot of three devices at a bias voltage equal to $V_{OC}$ (e) C-V plot under light and dark at 1 kHz frequency and (f) M-S plot under light and dark.
Figure 33: NP-OPV having $V_{OC} = 0.498$ V, $J_{SC} = 6.70$ mA/cm$^2$, $FF = 58.5$ and $\eta = 1.95\%$ (a) C-V measurement at 1 kHz frequency under varying illumination intensity. (b) M-S plot at 1 kHz frequency as a function of illumination intensity. As light intensity increases $V_{bi}$ decreases as well as carrier density increases (c) C-V measurement at 10 kHz frequency under varying illumination intensity. (d) M-S plot at 10 kHz frequency as a function of illumination intensity. As light intensity increases $V_{bi}$ decreases as well as carrier density increases. However, the change in carrier density is significantly less compared to the measurement carried out at 1 kHz frequency.
Figure 34: (a) Model fit to the experimental data for (a) BHJ-OPV device of PCE ~3.5%, (b) BHJ-OPV device of PCE ~ 2.7%, (c) NP-OPV device of separate nanoparticles of P3HT and PCBM (PCE~ 1.9%) and (d) NP-OPV device of blend nanoparticles of P3HT and PCBM (PCE ~2.0%). Solid lines are indicative of transmission line model for $L_n > L$ and broken lines are representative of Gerischer Model for $L_n < L$. 
Figure 35: Impedance plot of BHJ-OPV device (PCE ~ 2.7%) and NP-OPV device (PCE ~ 1.9%) under AM1.5G solar simulator at 100 mWcm\(^{-2}\) light intensity at (a) bias voltage 100 mV, (b) bias voltage 400 mV and (c) bias voltage equal to \(V_{OC}\) of the respective devices. (d) Transmission line model for BHJ-OPV showing \(R_{tr}, R_{rec}, C_\mu,\) anode and cathode impedance.

Table 2: Parameters to fit experimental data from the impedance measurement under 100 mWcm\(^{-2}\) light illumination at different bias voltages \(R_s, R_{co},\) and \(C_{co}\) values are not listed here.

<table>
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<tr>
<th>Voltage</th>
<th>(R_{se}) or (R_c) (Ohm)</th>
<th>CPE(-T) (F)</th>
<th>CPE(-P)</th>
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<tbody>
<tr>
<td></td>
<td>NP-OPV</td>
<td>BHJ</td>
<td>NP-OPV</td>
</tr>
<tr>
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<td>1.14E-8</td>
</tr>
<tr>
<td>400 mV</td>
<td>886</td>
<td>278</td>
<td>8.35E-9</td>
</tr>
<tr>
<td>@ (V_{OC})</td>
<td>1760</td>
<td>1746</td>
<td>6.75E-9</td>
</tr>
</tbody>
</table>
Figure 36: (a) $J$-$V$ curve of four different samples with different short circuit current and open circuit voltages. (b) Corresponding impedance plot of all four devices at 200 mV bias voltage. (c) Impedance plot at a bias voltage equal to $V_{OC}$ of the respective devices.

Figure 37: Impedance plot of blend NP sample and separate NP sample under AM1.5G solar simulator at 100 mWcm$^{-2}$ light intensity at different bias voltages (a) 0 mV, (b) 100 mV, (c) 300 mV and (d) at an applied voltage equal to $V_{OC}$. Symbol is representative of experimental data whereas lines represent equivalent circuit model fit.
Figure 38: (a) Capacitance and (b) resistance measurement of BHJ-OPV and NP-OPV devices.
Figure 39: (a) $R_{\text{rec}}$ or $R_G$ parameter extracted by fitting the IS data for BHJ-OPV and NP-OPV device having $V_{OC} = 0.58$ V and 0.45 V respectively. (b) chemical or bulk capacitance of the active layer either BHJ-OPV or NP-OPV calculated from fitting of IS data using equivalent circuit shown in the inset. $R_1$ and CPE-1 represent the interface resistance and capacitance while $R_2$ and CPE-2 represent the bulk properties of the polymer BHJ-OPV or NP-OPV.
Figure 40: Intensity dependent free carrier lifetime estimated from the impedance data for BHJ-OPV and blend NP-OPV at 0 V and 200 mV applied bias. Dotted line (slope = 1) indicates the bimolecular recombination mechanism.
CHAPTER 4

INTERPLAY BETWEEN ION TRANSPORT, APPLIED BIAS, AND DEGRADATION UNDER ILLUMINATION IN HYBRID PEROVSKITE P-I-N DEVICES

4.1 Abstract

We studied ion transport in hybrid organic– inorganic perovskite p-i-n devices as a function of applied bias under device operating conditions. Using electrochemical impedance spectroscopy (EIS) and equivalent circuit modeling, we elucidated various resistive and capacitive elements in the device. We show that ion migration is predictably influenced by a low applied forward bias, characterized by an increased capacitance at the hole-transporting (HTM) and electron-transporting material (ETM) interfaces, as well as in bulk. However, unlike observations in n-i-p devices, we found that there is a capacitive discharge leading to ion redistribution in the bulk at high forward biases. Furthermore, we show that a chemical double-layer capacitance buildup as a result of ion accumulation impacts the electronic properties of the device, likely by inducing either charge pinning or charge screening, depending on the direction of the ion-induced field. Lastly, we extrapolate ion diffusion coefficients (≈10^{-7} cm^2 s^{-1}) and ionic conductivities (≈10^{-7} S cm^{-1}) from the Warburg mass (ion) diffusion response and show that, as the device degrades, there is an overall depletion of capacitive effects coupled with increased ion mobility.

4.2 Introduction

Hybrid organic-inorganic perovskites (HOIPs) have emerged as an important class of materials for a diverse array of applications, ranging from photovoltaics to memory storage.\textsuperscript{183-184} An important feature of HOIPs is that they are mixed ionic-electronic conductors.\textsuperscript{183} Unique behaviors emerge when electron transport is modulated by ion transport or when ion transport is modulated by electron transport. This interplay between ionic and electronic transport has been implicated as the cause of many important characteristics of HOIPs, such as instability to light and heat,\textsuperscript{100, 185} hysteresis in current-voltage curves,\textsuperscript{186-188} switchable photovoltaic effects,\textsuperscript{189} thermoelectricity,\textsuperscript{190} and increased power conversion efficiencies.\textsuperscript{191} Thus, the interplay of electronic and ionic charge transport can significantly influence the functions of perovskites. Understanding the relationship between these processes is, therefore, critical to developing new HOIPs with improved stability and superior device performance for energy harvesting as well as other electronic applications.

Electrochemical impedance spectroscopy (EIS)\textsuperscript{192-195} is a powerful, non-destructive method to study charge and mass (ion) transport processes in mixed ionic-electronic conductors. Examining the current response over a range of AC voltage frequencies in EIS allows separation of processes that occur on different time scales, making it ideal for separating electronic and ionic processes in mixed conductors. EIS also provides information about charge and mass transport through the bulk as well as at grain boundaries and interfaces. EIS has been used to study HOIPs and these pioneering studies have shown the effect of device architecture, crystal size, and interface on the
transport processes that occur in HOIPs. Yet, there is still no comprehensive map of ion transport in HOIPs under device operating conditions.

Here, we systematically investigate the effect of DC applied bias on ion transport in HOIP photovoltaic devices under illumination using EIS. We used a planar heterojunction device with p-i-n architecture composed of methylammonium lead iodide (MAPbI₃) perovskite with poly(3,4-ethylenedioxythiophene)–polystyrenesulfonate (PEDOT:PSS) as the primary hole transporting material (HTM) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as the electron transporting material (ETM). We also examine the impact of related factors such as photo-degradation of the device, interfacial characteristics, and fabrication method on ion transport under these conditions. We see evidence of ions accumulating at interfaces under a low applied bias, consistent with our expectation and other experimental and theoretical studies. However, at high forward biases, contrary to expectations, we found that there is a capacitive discharge leading to ion redistribution in the bulk.

4.3 Experimental

4.3.1 MAPbI₃ Devices

Photovoltaic devices were fabricated as previously reported with minor deviations as follows: Poly(3,4-ethylenedioxythiophene)–polystyrenesulfonate (PEDOT:PSS) (Clevios PVP AI 4083) was filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter (Wilkem Scientific), and was spin coated onto ITO coated substrates (∼20 Ω sq⁻¹) at 2500 rpm for 30 s. A solution of lead iodide, PbI₂, in dry N,N-dimethylformamide (DMF) (400 mg mL⁻¹) was filtered through a 0.45 μm PTFE (Wilkem Scientific) filter and then heated to ∼80 °C. This hot solution was spin coated at
6000 rpm onto a hot PEDOT:PSS-coated substrate (∼80 °C) for 35 s. MAI was dissolved in isopropyl alcohol (40 mg mL⁻¹) and was spin coated onto PbI₂-coated substrates at 6000 rpm for 35 s at room temperature. The resultant MAPbI₃ samples were annealed (85 °C) for 45 min. A solution of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) in chlorobenzene (20 mg mL⁻¹) was spin coated atop the devices at 1000 rpm for 60 s followed by 2500 rpm for 10 s inside a N₂ filled glovebox (<1 ppm O₂, <1 ppm H₂O). A 15 nm thick Calcium electrode was thermally deposited at chamber pressure of 1 × 10⁻⁶ mbar followed by 100 nm of aluminum electrode. The power conversion efficiency of the freshly-prepared device was measured to be ∼11.5%.

4.3.2 Characterization

Current–voltage (J–V) curves were taken under an AM 1.5G solar simulator at 100 mW cm⁻² light intensity inside a N₂ filled glovebox. J-V scans were obtained from -0.5 to 1.5 V at a scan rate of ~ 0.26 V s⁻¹.

EIS of devices was measured under illumination at 100 mW cm⁻² AM1.5G simulated solar light with variable applied DC bias voltages. AC amplitude was kept constant at 20 mV and the frequency (ω) was swept from 100 Hz to 1 MHz. The impedance data from 100 Hz to 0.2 MHz were fit to an equivalent circuit model and the values of the circuit elements were obtained through a least-squares refinement.

Powder x-ray diffraction (PXRD) measurements were made using a PANalytical X’Pert3 X-ray diffractometer with a Ni filter, 1/2 in. diverging slit, vertical goniometer, and X’Celerator detector. Measurements were taken from 2θ = 10°–50° under Cu Kα (1.542 Å).
4.4 Results and Discussion

EIS results are plotted by convention as Nyquist plots (Cole-Cole plots), with the real component of the impedance ($Z'$) as the abscissa and the imaginary component ($Z''$) as the ordinate. The data closest to the origin are associated with the higher frequency spectrum whereas the data farther from the origin are associated with the lower frequency spectrum. The Nyquist plots of our HOIP-based device under light at various PCEs and applied DC biases are shown in Supplemental Figure 47. The Nyquist plots of HOIP-based devices generally consist of high frequency and low frequency components. Each component in the Nyquist plot can be modelled with a simple resistance-capacitance (RC) circuit. However, the low-frequency component requires a constant phase element (CPE) with an exponent ($\alpha \approx 0.5$) much lower than unity to fit the experimental results.

The observed large capacitance value under illumination has been attributed to charge accumulation at the interface, a giant dielectric constant, or ion transport. We observed a gradual degradation of MAPbI$_3$ to PbI$_2$ under heat and illumination (Supplemental Figure 48), indicating that the organic counterions (MA$^+$) may diffuse towards the electrode. Furthermore, in previous studies we have shown a dependence of the low-frequency component on the size of the organic counterion. We therefore surmised that ion accumulation at the electrode interfaces building up a double layer may be the origin of this large capacitance value. Our hypothesis is consistent with similar observations in EIS measurements of mixed ionic-electronic conductors. Therefore, we added a Warburg constant phase element to the equivalent circuit model for the low frequency component to account for ion transport. To verify the Warburg impedance in our devices, the imaginary ($|Z''|$) and real ($|Z'|$) components of $Z(\omega)$ were plotted as a
function of $\omega^{-1/2}$, as shown in Supplemental Figure 49, where the slopes are equal to the Warburg impedance ($A_W$). The extrapolation of $|Z'|$ to $\omega^{-1/2} = 0$, intersecting the ordinate at zero, clearly indicates the presence of a Warburg diffusion process.

The complete equivalent circuit model is shown in Figure 41. We have used this model in our previous studies, where we also analyzed several equivalent circuit models and showed that the model depicted in Figure 41 is robust for our devices. Our Warburg model for analyzing EIS data of HOIPs has also been independently validated by Fan and co-workers. In our circuit model, the high frequency component in the Nyquist plot is represented by a combination of recombination/transport resistance ($R_{tr}$) and a geometric or bulk capacitance ($C_{geo}$). Warburg diffusion is always associated with interfacial charge transfer resistance ($R_{ct}$) arising from imperfect electrode contacts and a double layer capacitance ($C_{dl}$) due to ion accumulation. Electronic resistance ($R_{electr}$) in parallel to the bulk capacitance ($C_{geo}$) captures charge transport/recombination originating from the electronic charge carriers (free electrons and holes) that are not coupled to ion diffusion/accumulation at the interface. $R_S$ is the series resistance of the device. Using Z-View 3.4c (Scribner Associates Inc.), we fit the experimental EIS data to this model using least-squares refinement. Values for the circuit components and $\chi^2$ (goodness-of-fit) for two-step devices are given in Supplemental Table 4.
Figure 41: (a) Example of an EIS response plotted in complex space for the 11.5% PCE device. The high frequency (left) portion of the plot shows a semicircle attributed to fast ionic/electronic conduction processes and the low frequency portion (right) side shows a linear portion ~45° from the origin attributed to ionic mass diffusion. (b) The equivalent circuit model used to fit all data. Details of each element are described in the text.

We used this equivalent circuit model to analyze EIS spectra to characterize ion diffusion in planar MAPbI$_3$ devices as a function of applied bias and device degradation. We calculated ion diffusion coefficients ($D$) from Warburg time constants ($T_w$) and ionic conductivities ($\sigma_{ion}$) from Warburg resistance ($W_r$). We also analyzed the trends in these values and in the capacitive and resistive elements to comprehensively understand ion migration in HOIP devices.

Our results show that the devices have three distinct response regions: in the low (0-400 mV), medium (400-600 mV), and high (>600 mV) levels of $V_{app}$. We will henceforth refer to these bias ranges as low, medium, and high $V_{app}$. We found that the trends in the circuit elements at low and high biases are opposite. An inflection point is seen at medium biases and the bias at inflection point closely corresponds to the voltage at maximum power point of the devices ($V_{max}$). We attribute these trends to ion migration through the bulk and ion accumulation at the interfaces, which is initiated by illumination.
and affects the electronic characteristics of the devices. The degradation of the device over time decreases the ability of ions to respond to applied bias and illumination.

We used a model introduced by Cameron, Peter and coworkers as the basis for analyzing our results. They suggested that in a n-i-p HOIP device under illumination, a large photovoltage \( V_p \) of \( \sim 0.5 \) V is introduced by photocarriers in a direction that opposes the original built-in field \( V_{bi} \), effectively discharging ions that have accumulated as a response to the \( V_{bi} \) under dark conditions. In our experiments, we apply a forward bias to HOIP devices under illumination. Therefore, we are applying a field that adds to the existing \( V_p \). This added field induces further redistribution of ions throughout the bulk. It would follow from the Cameron, Peter and coworkers model that as we increase the applied bias \( V_{app} \), we will eventually reach a point where the sum of \( V_p \) and \( V_{app} \) will become equal to \( V_{bi} \). At this point, there will be no net directional driving force for the ion to migrate. We designate this net driving force as \( V_{net} \). Increasing \( V_{app} \) beyond this point will result in a reversal of the driving force leading to ion accumulation at the opposite electrodes of the device. As the ions start to accumulate there is a build-up of Coulombic potential. At the inflection point, Coulombic potential is higher than the applied potential, which leads to the redistribution of ions in the bulk, effectively discharging the double layer capacitance (Figure 42). This hypothesis is also consistent with a model proposed by Snaith, Lin, Johnston and coworkers, where they invoked ion accumulation at the HOIP-electrode interfaces to explain why perovskite solar cells can function efficiently even without an ETM.
Figure 42: (a) Schematic of the response in a HOIP device under varying applied bias ($V_{app}$). The photo-induced voltage ($V_p$) and built in voltage ($V_{bi}$) remain constant at low $V_{app}$, thus, $V_{net}$ must fluctuate to maintain equilibrium. $V_{net}$ flips to oppose the $V_{app}$ at 400 mV, when the capacitance-voltage relationship indicates ion accumulation beginning to switch direction. $V_{net}$ continues to increase to compensate for increasing $V_{app}$ until the inflection point (600 mV) when ion accumulation alters the $V_{bi}$, inducing ion discharge at higher biases. (b) A qualitative representation of the magnitude shifts in $V_{net}$ as a function of $V_{app}$. The point at 400 mV where $V_{net}$ is neither opposing the $V_{bi}$ (-$V_{bi}$) nor in the direction of $V_{bi}$ (+$V_{bi}$) occurs when the sum of $V_p$ and $V_{app}$ equals the $V_{bi}$. Increasing the bias further requires $V_{net}$ to change direction to compensate the increasing electric field.

4.4.1 Bias-Dependent Analysis

The EIS results for the device under illumination at $V_{app} = 0$ V is shown in Figure 41. Powder X-ray diffraction of the MAPbI3 is shown in Supplemental Figure 50 and indicates a small amount of PbI2 is leftover in the film. Device characteristics extrapolated from $J$-$V$ analysis are shown in Supplemental Table 5. From the equivalent
circuit model, we determined the bulk capacitance ($C_{geo}$) to be $\sim 3$ nF and the interfacial double layer capacitance ($C_{dl}$) to be $\sim 0.3$ µF respectively, at $V_{app} = 0$ V (Figure 43). The capacitive effects are largely ionic in nature and can be ascribed to ion buildup at the interfaces. This hypothesis has been successfully used to explain the origin of J-V hysteresis in HOIPs. We found that at low $V_{app}$, there is minimal change to either $C_{geo}$ or $C_{dl}$ in devices with a certain degree of active layer degradation. In the device with the highest power conversion efficiency (PCE) of 11.45%, we found that both the $C_{dl}$ and $C_{geo}$ increase as a function of $V_{app}$ in the low range.

![Figure 43: Values for EIS equivalent fit circuit elements plotted as a function of DC bias at different device power conversion efficiencies. The legend for all PCEs can be found (top right): (a) double-layer capacitance ($C_{o}$) represents the low-frequency capacitive response at the ETM/HTM interface and is seen to increase as ions are biased initially, then decrease again at higher biases. As the device degrades, a shift in inflection point and a decrease of maximum capacitance indicate deeper ion trap states. (b) Bulk capacitance ($C_{bulk}$) models high-frequency and bulk capacitance arising from fast ionic/electronic charge distribution in bulk and follows the same trend as (a). Data from (a) and (b) are fit with Gaussian functions. Error bars for fits are shown. If error bars are not seen it is because the error was less than 5%, and the bars have been obscured by the data point.

At medium $V_{app}$, we found that there is a steady increase in $C_{geo}$ and $C_{dl}$, indicating that ions have begun accumulating at opposite interfaces (cations at the ETM and anions at the HTM) creating a new double layer, consistent with our hypothesis.
At medium $V_{app}$, $C_{dl}$ increases by ~900%, peaking at $V_{app} = 0.6$ V, as opposed to the modest increase in $C_{geo}$ (42% increase), peaking at $V_{app} = 0.7$ V. As we continue to high $V_{app}$, we see a reversal in trends and a decrease in capacitance. We attribute this trend to the increase in effective $V_{bi}$ at the inflection point caused by the increased Coulombic potential due to ion accumulation at the interfaces. At higher applied biases, there is a discharge of the double layer. It is important to note that this decrease does not appear to approach 0 µF, indicating that despite the ionic discharge, there is still a measurable double layer. It is also important to note that the inflection point, following which $C_{dl}$ begins to decrease, occurs at a lower voltage than the $V_{oc}$ where one might expect to see this inflection. This may be due to charge accumulation altering the $V_{oc}$. We note that this value is consistently closer to the $V_{max}$ of the device (~0.7 V) observed in J-V curves than to the $V_{oc}$.

We then prepared a HOIP device using an alternate method (Note S1) which has a different $V_{max}$ and similar EIS trends were observed with an inflection point that corresponded more closely to the $V_{max}$ than to the $V_{oc}$ of the device. These observations indicate that there are large capacitive effects when the device is at the highest power output at $V_{max}$. Snaith and coworkers used a numerical drift-diffusion model to simulate hysteresis in perovskite solar cells. This model predicts that when ion accumulation occurs in the direction of the $V_{bi}$, effective charge screening occurs which leads to a higher photocarrier concentrations and fewer recombination events. From this analysis, we conclude that the highest power output in our devices is at the point where there is maximum ion accumulation inducing a field in the direction of the $V_{bi}$. We note that this bell-shaped curve was not observed by Pauporté and coworkers in HOIP devices.
containing mesoporous TiO2 as the ETM, indicating that the nature of the ETM and HTM may play a large role in ion accumulation behavior.\textsuperscript{223} Varying $J-V$ hysteresis responses across devices with p-i-n versus n-i-p architecture is well documented, further underscoring the need to consider device architecture when analyzing ion transport.\textsuperscript{221} The analysis of n-i-p devices is a subject of future study but outside the scope of this publication.

We observe that the maximum value of $C_{dl}$ appears at lower $V_{app}$ than the $C_{geo}$ maximum (Supplemental Figure 51). We expect that the bulk capacitance should be impacted by changes in ion distribution (and redistribution) within the bulk and should not vary with the double layer formation. Therefore, $C_{geo}$ should reach its maximum at a $V_{app}$ after the double layer has begun to discharge. Indeed, we see that the $C_{geo}$ maximum is broad and offset slightly from $C_{dl}$ towards higher $V_{app}$ indicating that the discharge of $C_{dl}$ is accompanied by a charge redistribution within the bulk.

To further confirm that this capacitive response is due to ion accumulation at the interfaces, we fabricated devices with a cationic, anionic or zwitterionic-based HTM and studied their EIS response as a function of bias. We fabricated these devices in a one-step method using a previously described procedure.\textsuperscript{105} Changing the HTM to a cationic poly(benzothiadiazole vinylene-alt-2,5-bis(5-(N,N,N-trimethylammonium bromide)hexyloxy)-1,4-phenylenevinylene), or anionic poly(benzothiadiazole vinylene-alt-2,5-bis(4-sodium sulfonate)butoxy)-1,4-phenylenevinylene) yields trends in capacitance similar to those in the PEDOT:PSS devices, but with a shifted inflection point to higher $V_{app}$ for the anionic HTM (Supplemental Figure 52). We expect that MA$^+$ ions will accumulate at the HTM at lower $V_{app}$ and, thus, we expect the anionic HTM to
be capable of counter ion exchange with MA+ ions, shifting the point of inflection to higher biases. In our prior studies, we have established that the anionic and cationic HTM do not act as adsorbing interfaces and the ions move to and from the boundary through ion exchange mechanisms. These devices also show low hysteresis in J-V curves regardless of the scan rates. On the other hand, the zwitterionic polymer (poly(benzothiadiazolevinylene-alt-2,5-bis((N-(3-sulfonato-1-propyl)-N,N-dimethylammonium)hexyloxy)-1,4-phenylenevinylene), showed significant J-V hysteresis as a result of a dipole-induced interaction between the freely rotating zwitterionic moieties of the HTM and accumulating interfacial ions. We consider this interface to be adsorbing for ions, which confirmed the interpretation of the low frequency features in the EIS response. We observed overall capacitive trends that are similar to the other HTMs with minor differences. The onset of $C_{dl}$ occurs at lower $V_{app}$ and there is a broad inflection point in the double layer capacitance-voltage curve which extends into high $V_{app}$. These observations are consistent with an interface that has strong adsorbing interactions with both MA+ and I-.\textsuperscript{105} The shift in bias-dependent capacitive trends with the changing of HTMs is a clear indication that we are capturing ion accumulation at this interface, strongly suggesting that MA+ is mobile in this system.

Interestingly, such bell-shaped capacitance-voltage curves have been observed in electrochemical studies of room temperature ionic liquids (RTILs) where the maxima of capacitance corresponds to the potential of zero charge for the electrode.\textsuperscript{224-225} These systems have been modeled using mean field theory with a value $\gamma$ representing the ratio of the average ionic concentration to the maximum possible local concentration.\textsuperscript{226} Thus, ion size, mobility, and packing parameters at the double layer play a crucial role in the
capacitance-voltage curves of these systems. In the case of RTILs, the inflection point is attributed to a stage where all voids in the double layer are filled and counter ions begin to line the electrode. Surpassing this stage leads to a decrease in capacitance.\textsuperscript{225} We concluded that this is not likely a scenario for our system, as we see an increase in ion mobility and $C_\mu$ at higher $V_{app}$, indicating a loosely packed double layer capable of redistributing ions into the bulk. Nevertheless, the similarities between capacitance-voltage measurements of RTILs and HOIPs underscores the high ionic mobility and the crucial role that ion migration plays in the operation of HOIPs.

The Warburg component of our EIS circuit model, which models ion diffusion processes, shows evidence of semi-infinite diffusion of ions under low $V_{app}$ transitioning to a finite adsorbing boundary at high $V_{app}$. Warburg impedance can be written as

$$Z(j\omega) = \frac{A_W}{\omega^{1/2}} - \frac{jA_W}{\omega^{1/2}}$$

where $A_W$ is the Warburg impedance, $\omega$ is angular frequency and $\omega = 2\pi f$, and $j^2 = -1$. Generalized Warburg diffusion $W_s$ is described by the equation:

$$W_s = A_W \frac{\tanh{(j\omega T_W)^p}}{(j\omega T_W)^p}$$

where $T_W$ is the Warburg time constant and the exponent $P$ is $\sim0.5$ for finite-length Warburg diffusion.\textsuperscript{227} State-of-the-art first-principle calculations indicate that iodide migration would occur on timescales $<\mu s$,\textsuperscript{76} much lower than the ms timescale where we observe the Warburg response; thus, we assume that the iodide migration response overlaps the electronic response in the high frequency (first) semicircle. Additionally, a change in Warburg response as a function of organic cation substitution
indicates that by analyzing the Warburg diffusion we are specifically observing kinetics of MA⁺ migration. At low applied bias, we see evidence of a Warburg response in the low frequency region indicative of semi-infinite mass diffusion characterized by a linear impedance response approximately 45° from the real axis. As $V_{app}$ is increased the linear portion of the Nyquist plot begins to curve back toward the real axis, which is characteristic of mass diffusion to either a reactive or adsorbing boundary. The characteristics of interfacial Warburg responses are explained in detail in a previous work. Since we do not anticipate an electrochemical reaction to be occurring between MA⁺ and the ETM interface, we propose that at higher $V_{app}$ the Warburg curvature back into the real axis indicates an adsorbing boundary and therefore finite diffusion. For a non-ideal boundary in a finite diffusion model, where we assume diffusion layer thickness ($L_d$) to be approximately the film thickness ($d$), the Warburg exponent can also give insight into the processes occurring at the interface. $P \rightarrow 1$ would be a purely reflective boundary, characterized as a vertical capacitive line after the 45° linear response, and $P \rightarrow 0$, is a purely absorbing boundary, characterized by curvature back to the real axis. Examination of the Warburg exponent in our system shows that there is a local minimum in the $P$ exponent (~0.4) at the point of highest capacitance (0.6 V), which indicates that the PCBM-HOIP boundary is slightly adsorbing to MA⁺ at medium biases. However, when $V_{app}$ is increased we see a discharge in the double layer capacitance and a resulting increase in the Warburg exponent $P$. Due to the relatively reduced hysteresis in planar p-i-n devices we suspect that, while the boundary may be slightly adsorbing at prolonged medium biases, we see from ion mobility calculations that it does not significantly affect bulk ion mobility under operating conditions. This
observation does not rule out deep ionic trap states at interfaces leading to degradation of the device, nor does it account for iodide migration to the PEDOT:PSS layer.

Analysis of the Warburg component in films where \( L_D \approx d \) gives us insight into ion diffusion to interfaces and, in the case of thin-films, the bulk, due to the diffusion layer thickness in the device approaching the thickness of the active layer. It is clear that MA\(^+\) ions become more mobile under higher biases, as we see a decrease in Warburg impedance (\( A_w \approx 3000 \) \( \Omega \) at 0 \( V_{app} \) to \( \approx 200 \) \( \Omega \) at 0.6 \( V_{app} \)) and Warburg time constant (\( T_w \approx 7 \) ms at 0 V and \( \approx 1 \) ms at 0.6 V). The increase in \( C_{dl} \) in the intermediate range of \( V_{app} \) suggests that while the ions may be more mobile in the bulk, there is an increase of MA\(^+\) buildup at the ETM-HOIP interface. Additionally, as the number of defect sites increase throughout the bulk, ions are expected to move more freely through these defects. We validate this hypothesis using the comparison of \( A_w \) to PCEs where we see a decreasing Warburg impedance as a function of device degradation (Figure 44) discussed in detail in the ensuing section.
Figure 44: (a) Warburg resistance ($A_w$) as a function of bias at different device PCEs. As the capacitive double layer begins to build (400 mV), resistance to mass diffusion begins to decrease as ions are biased in the direction of $V_{bi}$. (b) Warburg resistance ($A_w$) for each PCE scan at $V_{app} = 0$ V as a function of degradation. Resistance to mass transport decreases steadily as the device degrades, indicating ions become more mobile with increased defect sites. Data from (a) & (b) are fit with Sigmoid functions. Where error bars are not seen, the error is < 2% and the size of points obscures error markings.
From $T_w$ we can estimate ion diffusion coefficients ($D$) for MA$^+$ using the equation:

$$D = \frac{L_D^2}{T_w}$$

Where $L_D \approx 300$ nm, corresponding to the film thickness measured by profilometry. We report $D$ values on the order of $10^{-7}$ cm$^2$ s$^{-1}$ for MA$^+$ (Table 3) and see that the diffusion coefficients remain constant at lower biases, and steadily increase after $V_{app} = \sim 0.5$ V, as would be expected as ions are biased in the opposite direction. Also, we also did not observe any decrease in the $D$ values as $C_{dl}$ reaches its maxima. It is likely that we are capturing increased ion diffusion through the bulk, as well as overall equilibrium of the double layer. For instance, an ion contained in the double layer may still be more responsive to AC perturbation than one in the bulk, as it experiences increased repulsive Coulombic forces due to accumulation of ions with the same charge.

We can estimate ionic conductivity ($\sigma_{ion}$) from the equation:

$$\sigma_{ion} = \frac{d}{\alpha \times A_w}$$

Where $\alpha = 0.06$ cm$^2$ and is the electrode area. We calculate $\sigma_{ion} \sim 10^{-7}$ S cm$^{-1}$ for EIS scans at low $V_{app}$ and see that $\sigma_{ion}$ increases two orders of magnitude to $\sim 10^{-5}$ S cm$^{-1}$ as higher biases are applied, as anticipated from the increasing $D$ at higher $V_{app}$. Overall, we conclude that despite the buildup of an ionic double layer at the interface, ions through the bulk become significantly more mobile in response to higher biases, likely due to increased defect sites.
Figure 45: Ionic diffusion coefficients (black, left) calculated from the Warburg time constant and ionic conductivity (blue, right) calculated from the Warburg resistance for the device at 10.5% efficiency. Data from diffusion coefficients are fit with a Sigmoid function, and error is taken from the average error for $T_w$ fits. Ionic conductivity is fit as a Gaussian, and error is taken from the average $A_w$ fits.

The $R_{tr}$ term, indicating electronic charge transport and recombination in the bulk material, follows an opposite trend to that of capacitance, reaching a minimum in the medium $V_{app}$ range. The results at low $V_{app}$ are consistent with charge pinning that arises from electronic charge carriers stabilizing accumulated ions, effectively creating a double layer of ions and pinned charges. In the medium region of $V_{app}$, ions begin accumulating at interfaces favorable to charge screening and thus we anticipate a decreased $R_{tr}$ term. In conjunction with this hypothesis, at the point of highest capacitance we see a minimum in $R_{tr}$ indicating favorable charge screening in this range, lining up near the $V_{max}$ of the device. As the double layer capacitance discharges at higher biases, we see an increase again in $R_{tr}$.
Similar bias dependent trends were observed in a device fabricated using a one-step method, with variations in onset and magnitude of the observed responses. We have detailed the fabrication method and bias response comparisons in Note S1.

Table 3: Calculated ion diffusion coefficients ($D$) and ionic conductivity ($\sigma_{ion}$) for the two-step device at 10.4% PCE

<table>
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<tr>
<th>$V_{app}$ (mV)</th>
<th>$D$ ($cm^2s^{-1}$)</th>
<th>$\sigma_{ion}$ (S cm$^{-1}$)</th>
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4.4.2 Device Degradation

We performed bias-dependent EIS on a HOIP device as it aged, monitoring PCE as a measure device degradation. The device degraded from an initial PCE of 11.5% to a final measured PCE of 4.6%. We found similar trends in EIS parameters throughout the aging process, including the three distinct regimes of behavior: low, middle, and high $V_{app}$. However, differences in initial values and shifts in inflection point onset were observed.

The initial values of both $C_{geo}$ and $C_{dl}$ generally decrease with decreasing PCE. Both capacitances exhibit the same bell-shaped capacitance-voltage curves observed in the fresh device, but the capacitance maxima decreases in magnitude and shifts to a higher bias for both $C_{geo}$ and $C_{dl}$ as the device degrades below 8.8%. Thus, a higher bias is required to move the ions to the interfaces and also discharge the double layer once
$V_{app} > V_{bi} + V_p$. This indicates an increase in $V_{bi}$ as the device degrades. The peak in $C_{dl}$ is sharper at all PCEs than the peak in $C_{geo}$, indicating that regardless of degradation, the ions at the double layer respond more quickly than those throughout the bulk. Additionally, the height of the peak in relation to the initial values decreases for both $C_{geo}$ and $C_{dl}$. At the lowest PCE of 4.6%, the peak for $C_{geo}$ is barely discernable from the initial and final steady state values. This can be justified by considering both defect sites enhancing ion mobility at interfaces and an increasing number of ionic trap states as the device degrades.

Initial values of $T_w$, the Warburg time constant, decrease as the device degrades. This trend indicates that ions are moving faster in the degraded devices, likely due to the increase in defect sites or grain boundaries through which ions can move. The decrease in capacitance coupled with faster ionic motion indicates that while the ions can move faster by taking advantage of vacancy defects, the total number of mobile ions has decreased as larger numbers of ions become trapped in grain boundaries or at interfaces. The $T_w$ at all PCEs drops near the $V_{max}$, and this decrease occurs at higher biases as the device degrades. However, the $T_w$ at each PCE is more similar in the high bias regime than in the low or mid biases. This increase in mobility of ions is supported by the Warburg resistance, $A_w$, values, which decrease as the device degrades. $A_w$ also shows a similar decrease to $T_w$ around $V_{max}$, where values at each PCE become much closer at high bias. Warburg exponent $P$ values for all PCEs show a slight increase throughout the degradation process, indicating that the interfacial boundary becomes more reflective (less adsorbing) as the HOIP layer degrades. This is consistent with the decreased $C_{dl}$ observed with aging.
The value of $R_{tr}$ shows a relatively steady initial value at low biases at all PCEs, which decreases as the device degrades. At medium bias $R_{tr}$ decreases and reaches a minimum before increasing again at high bias. This minimum shifts to higher bias as the PCE decreases, consistent with the shifts in capacitance values at each PCE. $R_{ct}$ continues to be negligible through most values of $V_{app}$ throughout device degradation, with a similar increase around the same high $V_{app}$ at all PCEs.

At each PCE, we generated a Mott-Schottky plot by using the inverse geometric capacitance-voltage relationship (Figure 45). The slope of the linear response is a measure of p-doping density of electrical defects and the abscissa-intercept gives information about the flat band potential ($V_{fb}$). We see minimal change in device defect density across degraded devices at higher PCEs as the slope of the linear portions remain relatively constant. As the device degrades below a PCE of 7%, the slope increases, indicating an increase in p-type defects as a function of degradation. In devices with high PCEs, the $V_{fb}$ increases as the device degrades from 11.45% to 7.4% (Figure 45). These two observations indicate that the properties of the bulk remain relatively unchanged as a function of bias while the device is above 7% PCE but the electronic properties of the PCBM cathode interface are influenced significantly in these high efficiency devices. If we consider ion buildup as a contributing factor in these observations, we can conclude that the decreased ion accumulation at medium biases (in the direction of $V_{bi}$) can induce a higher $V_{fb}$ since a higher $V_{app}$ would be needed to compensate for the lack of beneficial additive ion accumulation. Alternatively, as suggested earlier, an increase in $V_{bi}$ as the device degrades would also account for this response. A large $V_{fb}$ in inefficient devices
suggests that there is less beneficial ion accumulation at interfaces, corroborated by the decreased capacitance for low PCE devices as well as the increased defect density.

Figure 46: (a) Mott-Schottky plot taken from inverse square of the geometric capacitance ($C_{geo}$). The negative slope gives us insight into the p-doping density of the HOIP, and the linear region that intersects the abscissa axis gives us information about the flat band potential ($V_{fb}$, dotted line). (b) Flat band potential extrapolated from (a) as a function of degradation where $K_B$ is Boltzmann constant, $T$ is temperature and $e$ is electronic charge. There is a rapid increase in $V_{fb}$ at higher PCEs that begins to equilibrate close to 1 V at PCEs below 7%. Data from (a) is fit to a Gaussian and data from (b) is fit with a Sigmoid function.
4.5 Conclusions

In conclusion, we have determined that ions in HOIP photovoltaic devices respond to bias and illumination in a predictable manner by diffusing through the bulk and accumulating at specific interfaces. When the sample is illuminated, a photovoltage is induced in the opposite direction of the $V_{bi}$, decreasing $V_{net}$, and causing the ions to migrate towards the opposite interfaces. When low forward biases are applied, the ions begin to diffuse steadily towards the opposite interfaces, with the magnitude of $V_{net}$ shrinking, and eventually reversing sign and increasing in the opposite direction (aligned with $V_{bi}$). The cations now begin to accumulate near the ETM and the anions near the HTM until the accumulation reaches a maximum, which corresponds to the inflection point in bias trends near the $V_{max}$. At this point, ion accumulation creates a strong field in the same direction as $V_{bi}$, giving the highest observed capacitance values both across the device ($C_{μ}$) and in the double layer at the interfaces ($C_{dl}$). Anions at the HTM stabilize the transport of positively charged holes to the HTM and destabilize electrons at this interface, decreasing recombination and increasing charge extraction. The reverse holds true for cation accumulation at the ETM, resulting in minimum charge transport resistance ($R_{tr}$). At high biases, ion accumulation induces an increase in $V_{bi}$ causing ions to redistribute back into the film, leading to a decrease in capacitance and an increase in $R_{tr}$.
4.6 Supplemental Information

Figure 47: Nyquist plots for device at different PCEs and biases
Figure 48: X-ray diffraction of MAPbI₃ taken as a function of (a) heating (b) and heating under illumination. The appearance of the lead iodide (001) peak at 12.65 2θ indicates that there is a heat and light activated migration of MA⁺ ions in devices. Reprinted from Bag, M.; Renna, L. A.; Adhikari, R. Y.; Karak, S.; Liu, F.; Lahti, P. M.; Russell, T. P.; Tuominen, M. T.; Venkataraman, D., Kinetics of Ion Transport in Perovskite Active Layers and Its Implications for Active Layer Stability. J Am Chem Soc 2015, 137 (40), 13130-7. Copyright 2015 American Chemical Society.

Figure 49: Real and imaginary portion of impedance for the device at 10.4% PCE plot against 1/(√ω)
Figure 50: Warburg time constant \((T_W)\) plotted as a function of applied bias for the two-step method. The errors bars were added in cases where error exceeded 5%.

Figure 51: Charge transfer/recombination resistance \((R_{tr})\) term had an error of less than 5% except for the device with 4.6% PCE.
Figure 52: Forward and reverse $J$-$V$ scan for a sample MAPbI$_3$ p-i-n device showing minimal hysteresis. The device had a PCE of $\sim$11.0\%.

Figure 53: Comparison of bulk capacitance ($C_{\text{bulk}}$, right axis) and double layer capacitance ($C_{\text{dl}}$, left axis) for the two-step method taken from EIS fits for the 10.5\% device. Both data sets were fit with Gaussian functions. Where error bars cannot be seen, the error is low and obscured by the point.
Table 4: J-V characteristics of two-step preparation method, scans were taken in a positive direction from -0.5-1.5V at a rate of approx. 0.26 V s⁻¹. Scans for each PCE were obtained after impedance runs.

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc (V)</th>
<th>J_sc (mA/cm²)</th>
<th>V_max (V)</th>
<th>P_max (mW)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
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Figure 54: Double layer capacitance ($C_{dl}$) for device with different HTMs, anionic & cationic (left axis) and zwitterionic (right axis). All data sets were fit with Gaussian functions.
Table 5: Diffusion coefficient values calculated from $T_w$ for the two-step method.

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<th>PCE (%)</th>
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<td>Bias (mV)</td>
<td>D (cm² s⁻¹)</td>
<td>D (cm² s⁻¹)</td>
<td>D (cm² s⁻¹)</td>
<td>D (cm² s⁻¹)</td>
<td>D (cm² s⁻¹)</td>
<td>D (cm² s⁻¹)</td>
<td>D (cm² s⁻¹)</td>
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<td>0</td>
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<td>4.10E-7</td>
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<tr>
<td>800</td>
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<td>8.12E-7</td>
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<tr>
<td>1000</td>
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<td>----</td>
<td>----</td>
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<td>2.52E-5</td>
<td>----</td>
<td>2.55E-5</td>
<td>1.92E-5</td>
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</tbody>
</table>

4.6.1 One-Step Device Fabrication

The HTM, ETM, and electrodes for the one-step devices were fabricated as described in the experimental section, but the perovskite active layer was prepared as follows. Pb(OAc)$_2$ and MAI were dissolved in dry DMF (400 mg mL$^{-1}$) at a molar ratio of 1:3. The solution was filtered through a 0.45 μm PTFE filter (Wilkem Scientific) at room temperature. This solution was then spin coated at 6000 rpm onto a hot PEDOT:PSS/ITO substrate (~80 °C) for 35 s inside an N$_2$ filled glovebox (<1 ppm O$_2$, <1 ppm H$_2$O). The films were then annealed in dark at 100 °C for 5 min in a glovebox. The reported device PCE is 5.1%.

4.6.2 One-Step Method Analysis

The Nyquist plots of the one-step method for preparing the active layer are similar to that of the two-step (Supplemental Figure 55). The data was fit from 100 Hz to 0.1 MHz. The parameters obtained from fitting the circuit model shown in the manuscript are
for download at DOI: https://doi.org/10.7275/R52805TR. The parameters follow the same trends for both $C_{\text{bulk}}$ and $C_{\text{dl}}$ as a function of applied bias. As observed with the two-step method devices, increasing the $V_{\text{app}}$ above 0.5 V causes the discharging of $C_{\text{dl}}$, which can be associated with ions redistributing in the direction opposing $V_{\text{bi}}$. Consistent with that hypothesis, the largest value for $C_{\text{bulk}}$ is measured at 0.6 V, after the $C_{\text{dl}}$ maxima, when the ion charge carriers redistribute in the bulk of HOIP layer. Also, the $R_{\text{tr}}$ decreases at $V_{\text{app}} = 0.3$ V suggesting favorable charge screening processes occurring at points of higher capacitance. A decrease in $A_w$ and $T_w$ is observed between $V_{\text{app}} = 0.4$-0.6 V because ions are being biased (Supplemental Figure 56). As the double layer starts to build at $V_{\text{app}} = 0.45$ V, we see an increase in $T_w$ likely due to the decreased thickness of the one-step film (200 nm) lending to more impactful interfacial capacitance response in the bulk.

The diffusion length, $L_D$, is estimated to be the thickness of the film, ~200 nm. We report $D$ values for MA$^+$ on the order of $10^{-8} - 10^{-7}$ cm$^2$ s$^{-1}$ and see that the diffusion coefficients are constant at lower biases until ~0.35 V, after which they reach a maximum at $V = 0.5$ V. This observation is expected as $V_{\text{net}}$ increases in magnitude. Additionally, calculated $\sigma_{\text{ion}}$ for the one step method is reported on the order of $10^8$ S cm$^{-1}$ (Supplemental Figure 57).

Next, we briefly compare the one-step method to the two-step method. We have used the two-step device at 5.7% PCE to compare because that is the closest PCE value to the one-step device (5.1%) while these scans were obtained (Supplemental Table 6). Comparing both methods reveals that ions in the one-step device move at a slower rate at any applied bias than in the two-step method based on observations of the diffusion coefficients ($D$) as measured by $T_w$ which are 1 order of magnitude lower in the one-step
devices as opposed to the two-step devices. Also, at lower biases, the $R_n$ is 4 times greater in the HOIP prepared by the one-step method (Supplemental Figure 56). This would suggest that decreased ion diffusion leads to less favorable charge screening than what was observed in the two-step devices. $C_{bulk}$ is ~0.5 times smaller for the one-step method devices in the range of low $V_{app}$, confirming that there is less charge buildup in the bulk of the one-step method (Supplemental Figure 56). $C_{dl}$, on the other hand, is almost the same for both methods in the low bias regime indicating initial charge buildup at the interface is the same (Supplemental Figure 56). As previously mentioned, this maximum occurs at a lower $V_{app}$ in the one-step method which closely resembles the $V_{max}$ of this device. One possible explanation for these observations is the presence of a smaller $V_{bi}$ in the one-step device, suggested by the lower $V_{oc}$ (0.66 V), which establishes the equilibrium between $V_{bi}$ and $V_{app}$ at a lower bias.
Figure 55: Nyquist plots for the one-step method at different applied biases.
Figure 56: EIS equivalent fit circuit elements for the one-step (blue hourglass) and two-step (green triangle) methods plotted as a function of bias. (a) Double layer capacitance ($C_{dl}$) is larger in magnitude for the one-step method with an inflection point shifted to lower biases. (b) Bulk capacitance ($C_{bulk}$) follows the same trend as (a). (c) Charge transport resistance ($R_{tr}$) for the one-step method begins to decrease at lower applied bias in conjunction with the capacitance buildup in that range. (d) Warburg resistance ($A_W$) for the one-step method show an increase while the double layer builds, decreasing again at middle biases. The one step method stays significantly smaller than that of the two-step method.
Figure 57: Calculated diffusion coefficient \((D)\) and ionic conductivity \((\sigma_{\text{ion}})\) for the one-step method. \(D\) and \(\sigma_{\text{ion}}\) values were fit to a Lorentzian and Sigmoid function respectively.

Table 6: J-V characteristics for one-step prepared device taken at 45 °C.

<table>
<thead>
<tr>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>(V_{max}) (V)</th>
<th>(P_{max}) (mW)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.667100</td>
<td>11.461125</td>
<td>0.519833</td>
<td>0.310385</td>
<td>67.659886</td>
<td>5.173085</td>
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A complete dataset of circuit parameters obtained by fitting the impedance spectra to the circuit model for device studied is freely available at DOI:

https://doi.org/10.7275/R52805TR.
CHAPTER 5

LIGHT-INDUCED DEGRADATION OF HYBRID ORGANIC-INORGANIC PEROVSKITES REVEALS AUTOCATALYTIC KINETICS AND INCREASED STABILITY WITH SUBSTITUTION OF LARGER ORGANIC CATIONS

5.1 Abstract

Hybrid organic-inorganic perovskites (HOIPs) have shown incredible promise as photovoltaic active materials, but their instability to light remains a major roadblock in realizing these applications.** Changing the organic cation has been shown to affect light-induced degradation. As a strategy for increasing the stability of these materials, we replaced varying percentages of methylammonium in the archetypical methylammonium lead iodide (MAPbI$_3$) HOIP with three significantly larger organic ammonium cations: imidazolium, dimethylammonium, and guanidinium. We successfully synthesized HOIPs with the same 3D perovskite structure as MAPbI$_3$ with substitution of the larger ions as high as 20-30%. These substituted HOIPs retained similar optoelectronic properties. We discovered that the light-induced degradation reaction in MAPbI$_3$ and the substituted derivatives is autocatalytic and calculated rate coefficients for this reaction. All of the substituted HOIPs showed slower light-induced degradation compared to MAPbI$_3$ – up to a 62% decrease in degradation rate coefficient – at all substitution percentages up to 20%. This work provides evidence that a high percentage of a variety of large ammonium cations can be substituted into the HOIP lattice without compromising its desirable optoelectronic properties. Insight into the autocatalytic mechanism of light-induced

** This chapter was adapted with permission from a manuscript in preparation authored by Christie L.C. Ellis, Hamza Javaid, Emily C. Smith, and Dhandapani Venkataraman.
degradation will be valuable for designing additional strategies to improve the stability of HOIPs. We also offer insights into how factors other than size which may influence degradation, such as hydrogen bonding. Overall, we have shown that substitution of methylammonium for the much larger imidazolium, dimethylammonium, and guanidinium cations in MAPbI₃ is a valid strategy for creating stable HOIP derivatives by slowing the rate of light-induced degradation.

![Figure 58: Substitution of methylammonium in methylammonium lead iodide for the larger imidazolium, dimethylammonium, and guanidinium cations leads to increased stability under light. A unique autocatalytic degradation mechanism has also been observed in this work.](image)

### 5.2 Introduction

Hybrid organic-inorganic perovskites (HOIPs) have emerged as a promising class of materials for a plethora of applications due to the unique and desirable properties which arise their combination of organic and inorganic features.¹⁷, ⁴⁵, ²²⁹-²³⁰ Photovoltaics have been one of the most prominent, as the power conversion efficiencies of HOIP photovoltaics have skyrocketed to match or surpass those of current commercial technologies in just a few years.¹⁸ The current record efficiency for a HOIP photovoltaic is 25.2%, and efficiencies of 28.0% have been reached using tandem HOIP-silicon photovoltaics.²⁴, ²³¹ HOIP photovoltaic devices can be made thin, lightweight, flexible,
and semi-transparent using low-temperature, solution-based, scalable fabrication methods, all while maintaining their high efficiencies.

HOIPs are a class of materials with ABX$_3$ stoichiometry, where A is the organic cation, B is a divalent metal cation, and X is a halide anion$^{232-233}$ The ideal 3D cubic perovskite structure, shown in Figure 59, consists of corner-shared BX$_6$ octahedra, with the A cation in the cuboctahedral hole. The archetypical HOIP for photovoltaics is methylammonium lead iodide (MAPbI$_3$). It has a slightly distorted tetrahedral perovskite structure at room temperature which undergoes a continuous second order transition to the ideal cubic structure at 327 K (54 °C)$^{234}$ HOIPs are ambipolar charge transporters, with high mobilities for both electrons and holes, as well as ion transporters, with evidence that both the halide anion and organic cation may be mobile.$^{68}$

One of the major roadblocks to commercializing HOIP photovoltaics is their instability to environmental conditions, such as heat, humidity, applied electrical bias, and light.$^{19,235-237}$ Stability under light is a particularly crucial problem to solve, as light exposure is by definition required for photovoltaic devices. Understanding how HOIPs interact with light has not been straightforward.$^{238-239}$ Many experimental techniques used to probe their structure and properties cannot be performed under light. Even when the technique allows for light exposure, it has become apparent that multiple structural and optoelectronic changes take place at a variety of time scales under light, causing samples to change over the course of the measurement.$^{240-241}$

This has led to an abundance of theories on how light causes HOIP degradation, with widely varied and often contradictory conclusions. Creation of electronic trap states under illumination has been proposed via a variety of mechanisms.$^{117-118}$ Another
proposed theory is that light-induced chemical reactions, either within the HOIP active material itself such as deprotonation or formation of methyl iodide, or with interfacial materials could lead to degradation.\textsuperscript{119-123} It has been proposed that light can activate the transport of halide ions and/or organic cations.\textsuperscript{92, 124-127} Theories on the effects of this ion migration on degradation are also varied, from creation of deep trap states at ionic vacancy sites or ionic double layers at interfaces to structural destabilization.\textsuperscript{73, 128-129} Some theories invoke multiple factors necessary for degradation to occur, such as heat plus light, water plus light, or oxygen plus light.\textsuperscript{100, 118, 124, 127, 130-131} HOIPs with the formamidinium (FA) cation substituted for MA in the A-site of the lattice have exhibited increased light stability across numerous studies.\textsuperscript{124, 132-134} However, there is similar debate around the exact mechanism by which FA increases stability. It is larger than MA, has a much smaller (near zero) dipole moment, and two amine groups capable of hydrogen bonding as opposed to the single amine group present on MA. These factors affect the structure and electronics of mixed MA\textsubscript{x}FA\textsubscript{1-x}PbI\textsubscript{3} perovskites, and have also been proposed to slow or stop light-induced ion transport.\textsuperscript{129} Overall, there is a clear need for systematic studies investigating the complex interaction between light and HOIP materials.

As more evidence accumulated supporting substitution with FA cations as a strategy for not only improving stability but also boosting efficiency and tuning properties in HOIPs, interest grew in replacing MA with organic cations even larger than FA.\textsuperscript{112, 242-245} To predict which ions would form the desired 3D (pseudo)cubic perovskite structure of known HOIPs used for photovoltaics, researchers initially relied on the Goldschmidt Tolerance Factor.\textsuperscript{246} This equation, developed originally for all-inorganic
perovskites, predicts which perovskite structure will form based on the radii of the A, B, and X ions. Using the radii of Pb$^{2+}$ and I$^{-}$ for the B and X ions, the Goldschmidt tolerance factor predicted that no A-site cation with a radius larger than 2.6 Å would form the desired (pseudo)cubic 3D perovskite structure as it would not be able to fit in the cuboctahedral cavity.$^{62}$ Instead, it would instead form a lower-dimensional perovskite structure. Methylammonium (2.17 Å) and formamidinium (2.53 Å) both have radii within this limit.

Researchers have theorized that there may be more flexibility in the Goldschmidt tolerance factor for HOIPs than their all-inorganic analogues because molecular ions have several properties which are not well-described using only an estimated radius, such as shape, dipole, and hydrogen-bonding.$^{247-249}$ However, initial experiments which tried to incorporate larger organic cations seemed to support this size limit, as these cations could only be inserted in grain boundaries or on the surface and not in the A-site of the crystal lattice.$^{250-253}$ Recently, though, researchers have discovered methods which allow these large cations to be incorporated in the crystal lattice.

Jodlowski et. al. substituted guanidinium (GA) for MA to fabricate a wide range of MA$_x$GA$_{1-x}$PbI$_3$ HOIPs.$^{254}$ They showed that GA was incorporated into the A-site of the lattice at substitution levels as high as 25% and were able to fabricate photovoltaic devices with >19% power conversion efficiency. These compounds showed increased stability under light, which they attributed to increased hydrogen bonding between GA and iodide. Ferdani et. al. substituted up to 5% MA in MAPbI$_3$ with FA, GA, dimethylammonium (DMA), azetidinium (AZ), and acetamidinium (AC); at larger substitution percentages, they observed phase segregation.$^{255}$ They observed increased
stability in these compounds, which they attributed to a decrease in iodide ion transport. Franssen et. al. substituted up to 15% DMA for MA using a lead acetate precursor solution and were able to fabricate photovoltaic devices with >12% power conversion efficiency.\textsuperscript{256} Kubicki et. al. substituted GA for either MA or FA in MAPbI\textsubscript{3}/FAPbI\textsubscript{3} perovskites using mechanosynthesis.\textsuperscript{257} While the 3D structure of the mixed FA/GA perovskites was unstable, the mixed MA/GA perovskites showed incorporation into the lattice up to 40% GA and an increase in carrier lifetimes.

In this work, we chose three large organic cations to replace MA, shown in Figure 59 – imidazolium (IA), dimethylammonium (DMA), and guanidinium (GA). We systematically fabricated samples with 0-100% substitution of MA and characterized these with powder x-ray diffraction (PXRD) and ultraviolet-visible (UV-Vis) absorption spectrophotometry to gain insight into how their structure and properties change with increasing substitution percentage. Simultaneously testing these three different cations allowed us to identify trends that correspond directly to ionic size as well as those where other factors, such as dipole or hydrogen bonding potential, have an influence. Additionally, testing the active material itself rather than a full photovoltaic device allowed for removal of complicating factors that could potentially cloud results.
Figure 59: Left: Ideal 3D cubic perovskite structure with ABX$_3$ stoichiometry, where A is an organic cation (blue-black ion in center of connected octahedra), B is a divalent metal cation (green ion in center of octahedra), and X is a halide anion (purple spheres on corners of octahedra). The archetypical HOIP photovoltaic material methylammonium lead iodide (MAPbI$_3$) was used as a starting material for this work. MAPbI$_3$ has a slightly distorted tetragonal structure similar to the cubic structure shown here. Right: Organic ammonium cations used in this work. The larger IA, DMA, and GA were used to replace MA as a strategy for increasing stability of these HOIP materials under light.

We found that, for substitution percentages up to 10-20% (depending on the cation), we achieved a 3D tetragonal MAPbI$_3$-like perovskite structure with the large ions incorporated into the lattice and without any quantifiable amount of secondary phases. This 3D mixed cation perovskite phase persisted up to 80% substitution alongside other lower-dimensional perovskite phases. At high substitution percentages (90-100%), they formed entirely lower-dimensional perovskites, primarily 1D chain structures previously observed in literature.$^{258-262}$

We found that the unit cell volume of these compounds increased with increasing substitution percentage, and that the overall volume increase trends roughly with the size of the ion. We also observed that the substituted compounds maintain broad light absorption similar to MAPbI$_3$ with a <1% change in band gap.
We then exposed these samples to light until they were fully degraded and tracked the kinetics of their degradation reaction using PXRD. We determined that the mechanism of the light-induced degradation for MAPbI$_3$ and all its substituted derivatives is autocatalytic. We calculated rate coefficients for this reaction and found that every one of the substituted derivatives up to 20% showed slower light-induced degradation than MAPbI$_3$. The maximum decrease in rate was observed in the 5% GA substituted sample, which degraded 62.48% slower than MAPbI$_3$. Although all three large ions slowed degradation, the decrease in rate did not trend directly with size, suggesting that other factors such as hydrogen bonding may contribute to the increased stability.

Our results validate substitution of all three large ions as a promising strategy for significantly increasing the stability of HOIPs under light. Direct comparison of these three different ions as a function of both size and substitution percentage allows us to identify trends which may point towards the mechanism of this increased stability. They also reveal an important insight into the autocatalytic mechanism of this degradation reaction, which will aid in continuing to design strategies to overcome this crucial roadblock.

**5.3 Results and Discussion**

**5.3.1 Fabrication and Characterization of Substituted HOIP Derivatives**

The three large ammonium cations chosen to replace methylammonium (MA, ionic radius = 2.17 Å) in the A-site of the archetypical HOIP MAPbI$_3$ were (in order of increasing ionic radius) imidazolium (IA) at 2.58 Å, dimethylammonium (DMA) at 2.72 Å, and guanidinium (GA) at 2.78 Å. We focused primarily on the effect of size, although
these ions do differ in other properties such as hydrogen bonding and dipole moment (more properties found in Supplemental Figure 64).

The Goldschmidt Tolerance Factor ($t$), which was developed to predict which perovskite structure will form based on the radii of a set of A, B, and X ions ($r_A$, $r_B$, $r_X$) is shown in the equation below:\[ t = \frac{r_A + r_X}{\sqrt{2} (r_B + r_X)} \]

It has been empirically established that a $t$ value of 0.9–1 will give a 3D (pseudo)cubic perovskite structure with ABX$_3$ stoichiometry, as with the all-inorganic perovskite SrTiO$_3$.\textsuperscript{263} This largely holds true for the common hybrid organic-inorganic perovskites (HOIPs) MAPbI$_3$ ($t = 0.912$) and $\alpha$-phase FAPbI$_3$ ($t = 0.987$, FA = formamidinium); the structure of MAPbI$_3$ is tetragonal at room temperature, but it often referred to as pseudocubic as it is close to cubic at this point and undergoes a continuous second order transition to its cubic phase at 327 K (54 °C).\textsuperscript{233-234} $t$ values outside of this range often result in lower-dimensional perovskite structures. Since $r_A$ is in the numerator of the $t$ equation, an increase in the size of the A cation will increase $t$. FA, which is smaller than the ions tested here with a radius of 2.53 Å, is already near the top of this range.

IAPbI$_3$ gives a $t$ of 0.998, at the upper limit where this structure is predicted to form. DMAPbI$_3$ and GAPbI$_3$ have a $t$ of 1.027 and 1.040, respectively. Therefore, they would not be predicted to form the 3D (pseudo)cubic structure. Maintaining this structure is critical for maintaining the desirable optoelectronic properties of MAPbI$_3$. The organic cation does not directly contribute to the valence or conduction band; all of the orbitals...
involved in these bands come from the Pb\(^{2+}\) and I\(^-\) ions.\(^{264-265}\) However, MA\(^+\) stabilizes the geometry which gives optimal overlap of these orbitals, and a change in lattice size or structure could change the overlap and orientation of the Pb\(^{2+}\) and I\(^-\) orbitals.

It has been hypothesized, however, that the Goldschmidt tolerance factor may not describe HOIPs as well as their all-inorganic analogues.\(^{247-249}\) The radius of a molecular ion cannot be calculated as exactly as an atomic ion. Most calculations of this radius assume free rotation, but factors such as a small cuboctahedral cavity, hydrogen bonding, or dipole-dipole interactions could all hinder free rotation and thus change the effective radius and assumed spherical shape of the ion. Thus, we hypothesized that it may be possible to form the 3D (pseudo)cubic perovskite structure with larger organic A-site cations even when \(t > 1\).

Our results support this hypothesis, as we were able to successfully synthesize thin films of HOIPs with all three of the large cations (IA, DMA, and GA) substituted for MA in the A-site of the 3D perovskite lattice. All of the substituted HOIPs showed peaks characteristic of the MAPbI\(_3\) tetragonal (pseudocubic) structure, with slight shifts corresponding to changes in size. Our films showed a \(<110>\) orientation, so the \(110\) peak, which appears at a 2\(\theta\) value of \(\sim 14^\circ\), was the most intense in the powder x-ray diffraction (PXRD) pattern. This peak was used to track the presence/absence of the 3D mixed perovskite phase, both initially and as these samples degraded. PXRD patterns of MAPbI\(_3\) along with 10% substituted IA, DMA, and GA samples are shown in Supplemental Figure 65.

IA-substituted compounds maintained the 3D perovskite structure up to 10% IA substitution with only small PbI\(_2\) impurity peaks arising from incomplete conversion
during fabrication. At substitution percentages greater than 10% IA, the 3D mixed perovskite phase was still present alongside lower-dimensional perovskite phases. The 3D phase remained the majority phase through 30% IA substitution (based on relative peak intensities). Some of this 3D phase remained through 80% IA substitution, at which point the peak disappeared in the 90% sample. 100% IA formed the 1D chain perovskite structure previously observed in literature. PXRD patterns of 100% IA, DMA, and GA substituted samples are shown in Supplemental Figure 66.

DMA-substituted HOIPs maintained the 3D perovskite structure up to 15% DMA substitution. PbI$_2$ impurity peaks were not observed in the DMA-substituted HOIPs. At substitution percentages greater than 15% DMA, the 3D mixed perovskite phase was still present alongside lower-dimensional perovskite phases. The 3D phase remained the majority phase through 20% DMA substitution. Some of the 3D phase remained through 80% DMA substitution, at which point the peak disappeared in the 90% DMA sample. 100% DMA formed the 1D chain perovskite structure previously observed in literature.

GA-substituted HOIPs maintained the 3D perovskite structure up to 20% GA substitution with only small PbI$_2$ impurity peaks coming from incomplete conversion during fabrication. At substitution percentages greater than 20% GA, the 3D mixed perovskite phase was still present alongside other lower-dimensional perovskite phases. The 3D phase remained the majority phase through 30% GA substitution. Some of this 3D phase remained through 80% GA substitution, at which point the peak disappeared in the 90% GA sample. 100% GA formed 1D and 2D perovskite structures previously observed in literature.
The substituted HOIPs did show broader peaks with lower intensity and higher background than the MAPbI₃ controls, indicating that they are less crystalline. While this is not ideal, it can be improved by fine-tuning the fabrication and annealing conditions.

Pictures of the substituted samples are included in Supplemental Figure 67. The majority of the substituted HOIPs turned the same black-brown color as the MAPbI₃ control, even up to high substitution percentages where we know that other phases coexist with the 3D perovskite. The higher substitution samples eventually give a fainter brown color. The 100% substituted samples were pale yellow for DMAPbI₃ and IAPbI₃ and bright yellow for GAPbI₃.

The amount of a particular ion which can be substituted into the lattice before any secondary phases are formed does not appear to decrease with increasing size. The smallest ion (IA) formed just 3D perovskite up to 10% substitution. The largest ion (GA) formed just 3D perovskite up to 20% substitution, 10% more than the small IA ion. DMA, of intermediate size, fell in the middle at 15%. However, all three ions showed this 3D perovskite phase as the majority phase up to a similar percentage (20% for DMA, 30% for GA and IA). The formation of secondary phases may be more strongly related to the formation energy and stability of these lower-dimensional secondary phases than the instability of the 3D perovskite structure.

A comparison of the PXRD patterns of 0%, 50%, and 100% DMA substitution is shown in Supplemental Figure 68. For DMA substitution percentages 20-80%, every peak can be attributed to either the 3D pseudocubic perovskite or 1D chain perovskite phase, suggesting these two phases coexist. IA substituted HOIPs behave similarly. GA substituted HOIPs, however, have more than one phase present at 100% substitution, and
have peaks in the mid-range substitution percentages which cannot be attributed to either the 100% phases or the 3D pseudocubic phase.

We also observed shifts of the (110) and (220) peaks to lower 2θ angles in the PXRD patterns of the substituted HOIPs, indicating an increase in lattice size. This increase was roughly correlated to size, as larger ions led to a larger shift. DMA did show a larger shift at lower substitution percentages (up to 20%) compared to GA, but these ions are much more similar in size (0.06 Å difference in ionic radius) than MA or IA is to either of them. GA had a larger shift than DMA at substitution percentages of 30%+. An example of the (110) peak shift in MAPbI₃ and the 20% substituted samples is shown in Figure 60. The peaks shifted further right with increasing substitution percentages for all three ions; the d-spacing between the (110) planes versus substitution percentage is shown in Figure 60. The spacing between these planes increases with increasing substitution for all three large ions – until ~15-20% substitution for IA and DMA and 40% substitution for GA – at which point it levels out to a relatively constant value.

This increase in lattice size, which trends with both ionic size and increasing substitution percentage, indicates that the large ions are incorporated into the A-site of the 3D lattice and not simply present in grain boundaries or on the surface. Additionally, the lattice size stays relatively constant even at high substitution percentages where we know that the lower-dimensional perovskite phases coexist with the 3D perovskite phase. This indicates that larger ions are not excluded in favor of a mixed 3D perovskite with lower substitution percentage even when other crystal structure pathways are present for the large cations.
The lattice parameters and increase in unit cell volume for all substituted compounds up to 20% were calculated based on PXRD data, shown in Figure 60 and detailed in Supplemental Table 7. As expected from the (110) and (220) peak shifts, the volume of the unit cell increases with increasing substitution percentage to accommodate the larger ions. The trends for DMA and IA seem to correlate to their size, as both increase at similar rates, but IA gives a smaller unit cell volume than DMA. GA, however, increases in unit cell volume much more slowly than DMA or IA at low substitution percentages but eventually reaches a volume greater than IA and similar to DMA. MAPbI₃ gave a unit cell volume of 985.27 Å³. At 20% substitution, IA gave a unit cell volume of 1001.87 Å³ (1.68% increase), GA gave a unit cell volume of 1003.55 Å³ (1.86% increase), and DMA gave a unit cell volume of 1004.74 Å³ (2.28% increase). Lattice parameters were only
refined up to 20% substitution, but based on the peak shifts of 30-40% GA it is likely that the GA-substituted HOIP lattices continue to expand to the largest overall value after DMA and IA volumes become constant.

Figure 60: (a) Shift of the (110) peak in MAPbI$_3$ (top) and HOIPs substituted with 20% IA, GA, and DMA. The peak shift to lower angles indicates an increase in lattice size, which generally trends with ionic size. DMA and GA are switched as GA is slightly larger, but the difference in DMA and GA ionic radii (0.06 Å) is much smaller than the gap between these two ions and MA or IA. (b) (110) planes in MAPbI$_3$. (c) d-spacing between the (110) planes versus increasing substitution percentages. Spacing between these planes increases along with substitution percentage to a point, after which it levels out. For IA and DMA, this happens at ~15-20%, with the larger DMA settling at a larger d-spacing value than the smaller IA. GA, the largest ion, starts out with a relatively small d-spacing compared to DMA or IA but eventually increases to approximately equal to/slightly larger than DMA at ~30%. (d) Increase in unit cell volume with increasing substitution percentage.
Ultraviolet-visible (UV-Vis) absorption spectroscopy was recorded for all of the substituted compounds up to 20% and the band gaps were calculated from Tauc plots of this data, shown in Supplemental Figure 69. While they showed a slight increase in absorption from 350-550 nm and a slight decrease in absorption from 550-750 nm, the overall absorption profile remained very similar for all substituted compounds. The calculated band gaps varied by <1% for all substituted compounds and did not show any significant trend. The calculated band gaps are listed in Supplemental Table 8. This maintenance of the band gap of MAPbI$_3$ in the substituted HOIPs, which is well-suited for photovoltaic applications, is promising for the viability of these new compounds.

5.3.2 Light-Induced Degradation Kinetics

We hypothesized that substituting MA in MAPbI$_3$ for the larger IA, DMA, and GA cations would improve the stability of these compounds under light. To investigate this, we exposed the 0-100% substituted thin films to a very bright (~ 5 Sun) LED light for 24 h and monitored their degradation. The high brightness was chosen in order to (1) accelerate the degradation reaction so that we could observe the entire degradation over the 24 h period and (2) ensure that light was the primary stressor in causing degradation over other environmental factors such as heat or humidity, since the experiments were carried out in ambient air. To determine whether these other conditions did cause any degradation over the 24 h period, control samples were kept in the dark in the same ambient conditions as the degraded samples. These did not show any degradation by PXRD analysis over the 24 h period, indicating that the degradation measured in the primary samples is light induced. Pictures of the samples before and after the 24 h light exposure as well as the dark control samples are included in Supplemental Figure 67.
After complete degradation, all of the films turned yellow. This color comes from a mix of bright yellow PbI₂, the primary degradation product of MAPbI₃, and the lower dimensional perovskites (IAPbI₃ and DMAPbI₃ are pale yellow compounds, GAPbI₃ is bright yellow). Pictures of the set-up for the light degradation experiments and the spectrum of the LED light are also included in Supplemental Figure 70 and Figure 71.

We used PXRD to track the light-induced degradation of the 3D perovskite structure by measuring the samples every 4 hours through a 24 h period and calculating the decrease in (110) peak area (the most intense peak of the 3D perovskite phase). We were able to rule out simple zero, first, and second order kinetic mechanisms using this peak area versus time data (shown in Supplemental Figure 73). We noticed a characteristic “S”-shape of all of the peak area versus time plots, an example of which is shown in Figure 61. This shape is characteristic of an autocatalytic reaction, where one of the reaction products acts as a catalyst to speed up the reaction. Autocatalytic decomposition in solid state systems can be fit to the following equation:

\[ a = \frac{a_0}{1 + e^{-k(t+t_c)}} \]

Where \( a \) = area of (110) peak, \( a_0 \) = area of (110) peak at time zero, \( k \) = rate coefficient, \( t \) = time (hours), and \( t_c \) = critical point. Using this to fit our peak area versus time data, we were able to obtain a rate coefficient \( k \) for the light-induced degradation reaction of each of the substituted derivatives. A schematic of how this reaction mechanism and equation lead to the observed “S”-shaped curve is shown in Figure 61. Rate coefficients were only calculated up to 20% substitution, as many of the higher substitution percentages degraded before 24 h and thus had fewer points; however, these
could be obtained in the future and fit to the same equation by gathering more data points at earlier times. All of the calculated rate coefficients and their percent change compared to MAPbI₃ can be found in Supplemental Table 9.

**Figure 61:** (a) Area of (110) PXRD peak vs time exposed to light for HOIPs with varying percentages of DMA. HOIPs substituted with all three ions showed these “S”-shaped curves, indicating an autocatalytic degradation reaction mechanism. (b) Schematic of the phases of the autocatalytic reaction which give rise to the “S”-shaped curves and equation fitting these curves. We extract a rate coefficient $k$ for the degradation reaction from the fitting for each of these samples.

We found that every one of the substituted derivatives up to 20% had a smaller $k$ – corresponding to a slower light-induced degradation reaction – compared to MAPbI₃. The $k$ numbers as a function of large cation substitution percentage normalized to their MAPbI₃ control are shown in Figure 62b below. All three cations showed a steep initial decrease in $k$ from ~0-5% substitution, after which they either leveled out or increased slightly. However, none ever went back up to the level of MAPbI₃. DMA compounds showed the smallest decrease in rate coefficients compared to MAPbI₃, with a maximum decrease in $k$ of 36.96% at 20% DMA substitution. The maximum decrease in $k$ for IA was 51.26% at 7.5% IA substitution. GA showed the largest decrease in $k$ of all of the large cations, with a maximum decrease of 62.48% with 5% GA substitution. Even the
smallest decrease in $k$ – 14.56% for 2.5% DMA substitution – represents significantly improved light stability compared to MAPbI$_3$. This is strong evidence supporting our hypothesis that substituting any of the three larger IA, DMA, and GA cations for MA would lead to more stable HOIP compounds.

Figure 62: (a) Normalized rate coefficients ($k$) for the autocatalytic light-induced degradation reaction of the substituted HOIPs. All three of the ions at every substitution percentage showed slower light-induced degradation than MAPbI$_3$. 5% GA showed the slowest degradation, a 62.48% decrease in rate coefficient from MAPbI$_3$. (b) Normalized rate coefficients ($k$) for formation of PbI$_2$ during the light-induced degradation reaction. Increasing percentages of GA and DMA formed PbI$_2$ more slowly than MAPbI$_3$, as expected from their slower degradation. IA, however, showed faster PbI$_2$ formation than MAPbI$_3$ despite degrading more slowly.

Interestingly, the decrease in $k$ did not directly correspond to increase in ionic size. The largest ion, GA, led to the most stable compounds at nearly all substitution percentages. However, the smallest of the three ions, IA, led to more stable compounds than the larger DMA. This indicates that factors beyond size must be considered in evaluating the impact of new organic cations on stability under light.

GA exhibits behavior which deviates from expected size trends both in initial structure and degradation kinetics. GA differs from the other compounds in that it has no dipole and has several more potential hydrogen bonding sites. In fact, the decrease in $k$
does trend with number of amine functional groups capable of hydrogen bonding. DMA (least decrease in $k$) has one, IA (middle) has two, and GA (largest decrease in $k$) has three. Size undoubtedly plays a role, however. DMA and MA have the same number of amine functional groups, with MA’s amine group less sterically hindered and more polarized; thus, MA can theoretically form stronger hydrogen bonds than DMA. Therefore, if only hydrogen bonding were responsible for the increase in stability, DMA substituted compounds would likely be less stable than MAPbI$_3$. Hydrogen bonding ability is difficult to quantify, however, as other factors such as higher rotational freedom of MA$^+$ compared to the other compounds could also affect bond strength.

Since PbI$_2$ is the primary degradation product of MAPbI$_3$, and we know that the substituted samples degrade more slowly than MAPbI$_3$, we might expect that the rate of PbI$_2$ formation would decrease with increasing substitution. The rate of PbI$_2$ formation showed was calculated based on fitting the area of the (001) peak versus time plot (which showed the same unique S-shape) and is shown as a function of organic cation substitution in Figure 62b. This does seem to be the case for DMA and GA. Both show slower PbI$_2$ formation than MAPbI$_3$, and the rate decreases more in GA than DMA, also consistent with trends in degradation rate. IA, however, shows the opposite behavior, with PbI$_2$ formation rate increasing as a percentage of IA substitution.

Rate of PbI$_2$ formation does not give a complete picture of degradation products, however, as alternate low-dimension degradation products can also form when these larger cations are introduced. Differences in formation energy and stability of these alternate products could influence the rates of formation of PbI$_2$ in addition to the overall degradation rate. We were unable to quantify the rate of formation for these 1D products.
since for the majority of the lower percent substitution samples this peak did not appear at all or did not appear until very late in degradation (values listed in SI Table 4), but general observations point to differences in 1D product formation between the three ions.

We observe that IA samples up to 10% substitution show no evidence of the most intense (110) peak from the 1D IA phase, while 12.5% - 20% IA substitution has this peak but its area does not seem to change with time of light exposure and is not strongly correlated to percent of IA substitution. DMA 0-15% samples did not show any evidence of the most intense (010) peak from the 1D DMA phase, except for a very small area peak which appears at 12-16 h and disappears at 20 h. 20% DMA, however, shows a 1D peak which degrades with increasing light exposure time. None of the 0-20% GA samples showed the most intense (120) 1D GA phase peak at 0 h. The 0-5% GA samples never showed this peak through the degradation, but it appears for the 20% sample at 4 h, the 10, 12.5, and 15% samples at 8 h, and the 7.5% sample at 12 h. Additionally, unlike the IA or DMA 1D peaks, the area of the 1D GA peaks for all of these samples increases with both increasing degradation and increase GA substitution percentage. This may point to a lower formation energy of 1D GA degradation products compared to PbI₂ which seems to be favorable given that GA shows the largest increase in stability.

To gain further insight into the mechanism of light-induced degradation, the reversibility of this reaction was investigated. Samples of MAPbI₃ and 7.5%, 10%, and 12.5% large cation substituted HOIPs where measured by PXRD, exposed to light for 4 h and measured again, then placed in the dark for 24 h and measure a final time (Figure 63). After the 4 h light degradation, MAPbI₃ (black curve in Figure 63a, b, and c) degraded to 79% of its initial value, significantly more than any of the substituted
samples, as expected. After resting for 24 h in the dark, MAPbI$_3$ recovered to 87% of its original value, indicating the partial reversibility of this reaction, as observed in previous studies.$^{124}$ However, none of the substituted samples showed any reversibility in their degradation, either staying constant or degrading slightly more. This points to a combination of both reversible and irreversible degradation factors which affect the substituted HOIPs differently than MAPbI$_3$. 


Figure 63: Normalized area of (110) peak in MAPbI$_3$ and HOIPs substituted with 7.5%, 10%, and 12.5% IA (a), GA (b), and DMA (c). The first point is initial value, the second is after 4 h of light-induced degradation, and the third is after 24 h of resting in the dark. MAPbI$_3$ degraded more than any of the substituted samples in 4 h. However, MAPbI$_3$ degradation was partially reversible, while the substituted HOIPs either stayed the same or degraded slightly more.
Light-activated ion transport could act as a reversible degradation mechanism.\textsuperscript{92, 124, 129, 269-270} The more stable substituted samples may show less ion migration out of the lattice compared to MAPbI\textsubscript{3} because of increased hydrogen bonding, increased activation energy for movement of larger cations, or passivation of grain boundaries as a path for ion movement. However, when the light is turned off, those ions which had moved out may be less to diffuse back into the substituted samples for the same reasons, while being able to diffuse back into MAPbI\textsubscript{3} much more easily.

Chemical reactions could act as irreversible degradation mechanisms, and it is logical that these different molecules would have different reactivities. One other study conducted by Pont et. al. observed autocatalytic degradation of mixed halide HOIPs under light in ambient air.\textsuperscript{271} They ruled out oxygen diffusion through the film as the cause for the delayed onset of light-induced degradation, instead hypothesizing that one of the degradation reaction products was acting as the catalyst. They noted, however, that films with bromide were much more light-stable than those with iodide. I\textsubscript{2} is a common reactive species invoked in HOIPs, but there is disagreement on how it is formed and how it reacts.\textsuperscript{272-276}

Fu et. al. identified an autocatalytic light-induced degradation reaction in FA\textsubscript{1-x}MA\textsubscript{x-Pb(I\textsubscript{y}Br\textsubscript{1-y})\textsubscript{3}} HOIP photovoltaic devices and assigned I\textsubscript{2} as the autocatalyst in their systems.\textsuperscript{276} They observed that their encapsulated devices ruptured from the built-up pressure of I\textsubscript{2} after a certain amount of light-induced degradation, while bare films showed greatly increased stability. They measured the gases which evolved from their system and found I\textsubscript{2} and CH\textsubscript{3}I. However, the reaction where I\textsuperscript{-} displaces NH\textsubscript{3} gas may not be able to proceed in a similar fashion with all of the compounds used in this work. DMA
could potentially react like this, with CH$_3$NH$_2$ as the leaving group rather than NH$_3$. IA and GA, however, have very different structures which would not react in this SN$_2$ fashion.

On the other hand, Wang et. al proposed that I$_2$ could form I$_2^-$ under light, which would react with CH$_3$NH$_3^+$ to form CH$_3$NH$_2$, I$_2$, and H$_2$. All of the species used in this work have protons which could be removed. We examined the pKa values for the ions used in this work. In order from most to least acidic were IA (6.95), MA (10.6), DMA (10.8), and GA (12.5). This does not exactly follow the degradation trends, as IA substituted samples degrade more slowly than MAPbI$_3$. However, it does trend with the rate of PbI$_2$ formation, so deprotonation may be involved in the pathway of the degradation reaction which forms PbI$_2$ as a product.

Light seems to be the primary driving factor for the accelerated autocatalytic degradation observed across these studies, in HOIPs with both mixed cations and mixed halides. Fu et. al conducted their work in an N$_2$ atmosphere under high heat (80 °C) and noted that the degradation would not proceed without light, but that even a low intensity light would trigger it. Pont et. al. observed the same autocatalysis, but at room temperature under ambient conditions with a very low intensity fluorescent light (∼2 mW cm$^{-2}$ intensity at 550 nm).

The interaction of light with HOIPs which leads to degradation is complex and multifaceted, but the increased stability of these new HOIP derivatives substituted with IA, DMA, and GA provides some new insights. There seems to be both a reversible and an irreversible component to the degradation. The substituted HOIPs appear to be affected by the irreversible mechanism but have a substantially reduced reaction to the
reversible mechanism. Reactive iodide species seem to be formed under light. Finding organic cations which do not undergo these irreversible reactions – either because of steric hindrance, increased pKa, or different molecular geometries – should increase stability. All of the cations tested here appear to still undergo chemical reactions to some extent, but the low pKa of DMA and GA may be contributing to their increased stability. Chemical reactions do not seem to be the only source of degradation in MAPbI₃, however, as a distinct reversibility is observed in these samples which is not present in the substituted derivatives. This reversible degradation seems to be the primary pathway which is avoided in the substituted HOIPs. An increased activation energy for ion transport with the larger ions may lead to this decrease in reversible light-induced degradation; this will be investigated in future works.

5.4 Conclusions

We successfully fabricated hybrid organic-inorganic perovskites (HOIPs) with 0-100% substitution of the methylammonium (MA) cation in archetypical MAPbI₃ with the larger imidazolium (IA), dimethylammonium (DMA), and guanidinium (GA) compounds. These substituted HOIPs maintained an MAPbI₃-like 3D pseudocubic perovskite structure as a primary or secondary phase up to high substitution percentages, despite predictions that these cations were too large to fit into the MA lattice site. These compounds showed increasing lattice size with increasing substitution percentage as well as with increasing ionic radius, confirming their integration into the lattice itself. This also suggests that ions with radii even larger than the largest ion we tested, GA (2.78 Å) could be substituted for MA to create new HOIP derivatives. The bands gaps of these compounds remained constant at the same value as MAPbI₃, which is well-suited for the
desired photovoltaic applications. After characterizing their degradation under illumination, we found that every one of the HOIP derivatives up to 20% substitution showed increased stability compared to MAPbI₃, with a maximum decrease in degradation rate of 62% for 5% GA substitution. We observed a unique autocatalytic mechanism of this light-induced degradation which will provide important insights into further understanding how these cations improve HOIP stability and how to design even more stable materials. We also noted how characteristics of the larger cations other than size, such as dipole and hydrogen bonding, may play a role in stability. This was especially noticeable for GA, the only ion with no dipole and three amine sites, which showed noticeable deviations from size trends in both structure and degradation kinetics. Overall, we have confirmed our hypothesis that substitution of IA, DMA, and GA for MA in MAPbI₃ HOIPs yield compounds with improved light stability which are promising alternatives for use in HOIP photovoltaic applications.

5.5 Materials and Methods

Lead (II) iodide (99.9985%) was purchased from Alfa Aesar. Methylammonium iodide, imidazolium iodide, dimethylammonium iodide, and guanidinium iodide were purchased from GreatCell Solar. PEDOT:PSS Al4083 was purchased from Ossilla. All chemicals were used as purchased.

Glass substrates were cleaned by sonicating 20 minutes each in DI water with detergent, DI water, acetone, and isopropanol, then drying at 150 °C for at least 2 hours. PEDOT:PSS underlayer was coated on glass substrates by treating substrates with UV-O₃ for 20 minutes, then spin-coating PEDOT:PSS solution filtered through 0.45 µm PTFE
filter onto substrate at 2500 rpm for 40 seconds. PEDOT:PSS was then annealed at 150 °C for 30 minutes.

1.5 M solutions of 1:1 MAI:PbI₂ and 1:1 LAI:PbI₂ (LA = large ammonium ion) in 7:3 gamma-butyrolactone: DMSO were prepared in an N₂-filled glovebox and dissolved by stirring overnight in dark at 60 °C. After fully dissolving, these solutions were mixed in varying ratios to make mixed MAₓLA₁₋ₓPbI₃ solutions.

Spin-coating was performed in an N₂-filled glovebox. 100 µL of MAₓLA₁₋ₓPbI₃ solution was coated onto PEDOT:PSS coated glass substrates at 2000 rpm for 80 s, dripping toluene anti-solvent at 40 s. The resulting films were annealed at 100 °C in the dark for 5 minutes.

Ultraviolet-visual absorption spectrophotometry was measured on thin films from 250 – 1100 nm on a Shimadzu UV-2401PC.

Samples were exposed to 5000 K LED light with ~5 Sun intensity for up to 24 h or until complete degradation of 3D perovskite phase occurred. The spectrum of the LED light is included in Supplemental Figure 72. This high intensity was chosen to accelerate complete light-induced degradation of samples to take place over a 24 h period. Samples were kept in ambient air at 35 °C and 35-45% RH. Dark control samples were kept in same ambient conditions.

All powder x-ray diffraction (PXRD) measurements were taken on a SmartLab SE powder diffractometer. Data was analyzed using the SmartLab Studio II software to remove background, identify peaks, calculate peak area, assign peaks to tetragonal structure, and calculate lattice parameters and unit cell volume. Lattice parameter refinement was done by whole powder pattern fitting (WPPF) method.
Degradation kinetics data (PXRD (110) peak area vs time exposed to light) was fit to the logistical equation described in the text using Origin 2019 to obtain rate coefficient $k$.

### 5.6 Supplemental Information

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Figure 64: Properties of large organic ammonium cations used in this work.

Figure 65: PXRD patterns of MAPbI\(_3\) and 10\% substitution of IA, GA, and DMA. All four maintained the MAPbI\(_3\)-like tetragonal 3D perovskite structure. The films were oriented in the \(<110>\) direction, so the (110) and (220) peaks were most prominent and present in all four samples. The (110) peak was used to quantify degradation of the 3D perovskite structure. Small PbI\(_2\) impurity peaks arising from incomplete starting material conversion are visible in GA pattern.
Figure 66: PXRD patterns of MA$_{0.5}$DMA$_{0.5}$PbI$_3$ (50% DMA substitution), MAPbI$_3$ (0% DMA substitution), and DMAPbI$_3$ (100% DMA substitution). Both the 0% and 100% phases are present together in 50% sample. This is similar for IA. GA has some unassigned peaks in mid substitution percentages.
Figure 67: Increasing % large cation (LA) substituted samples 0% = MAPbI₃, 100% = LAPbI₃. Thin films on PEDOT:PSS-coated glass substrates. a. and b. = DMA, c. and d. = IA, e. and f. = GA. Left (a, c, e): Freshly made samples. Right (b, d, f): Samples after 24 h. Samples on left in each cell have been exposed to light for 24 h, samples on right are controls that have been kept in the dark in same ambient conditions (ambient air, temperature, humidity). Dark controls showed no discernable degradation over the 24 h period by PXRD analysis.
Figure 68: PXRD patterns of 100% large cation substituted compounds (0% MA).
Table 7: Lattice parameters of 0-20% large cation substituted compounds

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Figure 69: Tauc plots from UV-Vis absorption data of 0-20% substituted films used to calculate band gap.
Table 8: Band gaps of substituted compounds calculated from Tauc plots of UV-Vis spectrophotometry data.

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<thead>
<tr>
<th>% Large Cation</th>
<th>IA Band Gap (eV)</th>
<th>GA Band Gap (eV)</th>
<th>DMA Band Gap (eV)</th>
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<tr>
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<td>1.552</td>
<td>1.554</td>
<td>1.549</td>
</tr>
<tr>
<td>5.0%</td>
<td>1.546</td>
<td>1.545</td>
<td>1.544</td>
</tr>
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<td>1.542</td>
<td>1.552</td>
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<tr>
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<td>1.543</td>
<td>1.548</td>
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</table>

Figure 70: MAPbI$_3$ and 5% substitution control samples at 0 h and after 24 h in dark.
Figure 71: Set-up for light-induced degradation kinetics experiments. a. LED array used as light source for experiments. b. Turntable (white) with wedge to hold samples. Turntable rotated at 1.6 rpm to ensure even illumination of all samples. c. Samples on turntable placed beneath housing which blocked out other light with LED array shining down from top and cooling fan on top of LED. Temperature under light with cooling fan was 35 °C.

Figure 72: Spectrum of LED lamp used in degradation experiments. Intensity was ~5 Sun.
Figure 73: Simple zero, first, and second order kinetic models were ruled out before applying more complex models.

Table 9: Rate coefficients $k$ of light-induced degradation reaction and percent decrease in $k$ for each substituted sample compared to its MAPbI$_3$ control (0% substitution shown in top row).

<table>
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<tr>
<th>% Cation Substitution</th>
<th>IA $k$ (h$^{-1}$)</th>
<th>% decrease in $k$ from MAPbI$_3$</th>
<th>DMA $k$ (h$^{-1}$)</th>
<th>% decrease in $k$ from MAPbI$_3$</th>
<th>GA $k$ (h$^{-1}$)</th>
<th>% decrease in $k$ from MAPbI$_3$</th>
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<td>0.43463</td>
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<td>0.37002</td>
<td>41.32%</td>
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Table 10: Area of most intense PXRD from 1D degradation product (IA = (110), DMA = (010), GA = (120)) as a function of time.

<table>
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<th>IA</th>
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<th>4 h</th>
<th>8 h</th>
<th>12 h</th>
<th>16 h</th>
<th>20 h</th>
<th>24 h</th>
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In Chapter 5, imidazolium (IA), dimethylammonium (DMA), and guanidinium (GA) were shown to improve HOIP stability under light by partially replacing methylammonium (MA) in the archetypical HOIP MAPbI₃. These ions were predicted to be too large to fit into the HOIP lattice by the Goldschmidt Tolerance Factor, but all of them were successfully incorporated into the 3D HOIP lattice. There are a plethora of other ions which could also be substituted for MA despite their large size which may lead to even greater improvements in properties like stability (some of these are shown in Figure 74 below).

**Figure 74:** Additional large organic cations to pursue as substitutes for MA⁺ in MAPbI₃ for increased light stability.

In addition to using these cation to generate a larger library of new materials, running these experiments on additional organic cations will allow further investigation
into how different molecular properties affect the stability of HOIPs under light. Ions which are similar in most properties but differ in one important way could be compared to narrow down the effect of properties like size, shape, weight, dipole, and hydrogen bonding. Examples of comparison sets are shown in Figure 75 and Figure 76.

**Figure 75:** Cations to compare against one another to determine the effect of different molecular properties on stability. Each set (a) and (b) are similar in size, shape, and weight but differ in dipole and number of hydrogen bonding sites.
Figure 76: Cations to compare against one another to determine the effect of different molecular properties on stability. Each set has the same number of hydrogen bonding sites but differ in size, shape, weight, and dipole.

While the IA, DMA, and GA substituted HOIPs showed little change in band gap or absorption edges, they did show differences in overall UV-Visible light absorption which seem to change based on the ion. All of the three ions showed a decrease in absorption in the 550-750 nm range and an increase in the absorption in the 350-550 nm range. However, the relative amount of change varies. DMA substituted samples barely change at all, while IA samples change dramatically, with GA falling in an intermediate position (shown in Figure 77). The origin of this difference in absorption could be investigated both for theoretical interest and to determine its potential impact on device performance.
Figure 77: Normalized UV-Visual light absorption of 0-20% DMA (a), IA (b), and GA (c), and MAPbI$_3$ vs. 20% substituted HOIP of each (d). Spectra are cropped to 0.8 – 1 to show small differences in top of absorption. All substituted HOIPs showed slight decreases in absorption in the ~550-750 nm range and slight increases in absorption in the ~350-550 nm range. However, DMA changed only slightly, GA changed slightly more, and IA changed fairly drastically.

Light-activated ion transport is a potential cause of degradation in HOIPs which our group has previously studied. We hypothesize that the increase in stability in the substituted HOIP compounds may be a result of an increase in activation energy for transport of the organic cation. We can quantify this using variable temperature EIS. However, I have thus far encountered challenges in getting clear enough measurements of these materials to accurately quantify this value. An example EIS spectrum taken of MA$_{0.8}$DMA$_{0.2}$PbI$_3$ (20% DMA substitution) is shown in Figure 78. While we see the two semicircles we would expect to see based on MAPbI$_3$ and other mixed ionic-electronic conductors, they are not resolved enough to model the Warburg component which describes ion transport. This increase in diameter of the semicircles is due to an increase in resistance. While this may be intrinsic to the new materials, it is more likely due to the experimental set-up. EIS of full HOIP PV devices typically shows low noise and the metal-deposited electrodes made good contact with the film. However, the EIS
instrument which we use to take measurements of full devices does not go to a very low frequency, and thus often does not capture enough of the spectrum to quantify ion transport, especially if it has been slowed even further. Additionally, the additional layers and interfaces in a device may complicate measurements; it would instead be desirable to measure just the HOIP material itself, either with electrodes only or with identical layers on either side such as the PEDOT:PSS used in previous work. However, these measurements are often taken by coating the HOIP material on one ITO-coated substrate and clamping another on top. This set-up often leads to increase noise and resistance. However, deposition of metal electrode on top of the HOIP film on ITO often leads to penetration of the metal through the film and shorting of the device. Troubleshooting of these measurements should continue or an alternative method to quantify ion transport in these systems should be found.
Figure 78: EIS spectra for MA$_{0.8}$DMA$_{0.2}$PbI$_3$ (20% substitution) at increasing levels of bias. Inset: schematic of theoretical EIS spectra of a mixed electronic-ionic conductor with a Warburg element which can be used to quantify ion transport. In these samples, the two semicircles are not resolved enough to determine if a Warburg element is present.

Finally, the potential of these new substituted HOIP materials for PV devices should be evaluated. My lab mate Hamza Javaid has already begun this work. HOIPs with large cations substituted have already been shown to form high efficiency devices (Figure 79) and the PV device characteristics provide another tool to study the properties of these new, promising derivatives.
Figure 79: J-V scans and PCEs of full PV devices made from HOIPs with 5% large ion substitution. Reverse and forward scans show degree of hysteresis for each of the substituted HOIPs.††

†† I gratefully acknowledge Hamza Javaid for the PV device efficiency data for the substituted HOIP samples.
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