REDUCING INTERFACIAL LOSSES IN PEROVSKITE SOLAR CELLS

by

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B.S., University of Virginia, 2016

A thesis submitted to the Faculty of the Graduate School of the University of Colorado in partial fulfillment of the requirement for the degree of Doctor of Philosophy Department of Chemistry 2023

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Abstract

Metal-halide perovskites possess an unprecedented combination of electronic and optical properties resembling those of traditional inorganic semiconductors yet can be processed at low temperatures from solution. Additionally, these materials have short estimated energy payback times and high potential for integration into tandem-on-silicon solar cells. The latest record single junction perovskite solar cell has reached a certified efficiency of 25.8% and perovskite-silicon tandem solar cells have reached an efficiency of 33.7%. Nevertheless, numerous research challenges remain towards commercialization, including efficiency, stability, scalability, and Pb toxicity. The research within this thesis focuses on a materials driven approach to reduce non-radiative losses in perovskite photovoltaics for single junction and tandem-on-silicon applications.

I will first describe the synthesis, characterization, and material properties an NDI side chain copolymer incorporating cinnamate crosslinking groups. We demonstrate the polymer's high transparency, thermal stability, photocrosslinking, and n-doping via solution and sequential processes. We implement this polymer in PSCs and characterize its solar-cell device performance relative to an uncrosslinked homopolymeric counterpart in n-i-p devices with a MA-free perovskite absorber. Next, I will discuss a large photoluminescence-based screening of passivation materials. Candidate passivators were screened across a variety of perovskite compositions. A benzylammonium trifluoromethanesulfonate salt, BAOTf, was identified as a highly effective passivation molecule, allowing for the fabrication of solar cells exhibiting very low hysteresis with PCEs >19% with a MA-free mixed-cation mixed-halide perovskite absorber (Cs17Br25). Finally, the reactivity of amines and ammoniums with formamidinium salts was explored. Understanding solution reactivity of amines with formamidinium salts enabled the

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synthesis, isolation, and implementation of the product(s) formed in these reactions as additives and surface passivation agents in perovskites. This work helped to elucidate the role of the amine/ammonium additives in controlling FA-containing perovskite growth and crystallization processes.

Acknowledgements

I want to thank my advisor, Professor Seth Marder for his constant scientific and personal support during my time as a graduate student. I learned to be a more thoughtful scientist through many "Marderizations" and many more informal discussions of my research ideas. After more than five years of working together, I'm still amazed by your creativity and ability to solve scientific problems so quickly and tactfully. Your support of my personal and scientific development has afforded me many opportunities and been instrumental in shaping me into the scientist I am today. Thank you for never giving up on me and pushing me to do scientifically robust and rigorous work.

I am also grateful to Professor Stephen Barlow. Your ability to distill complex scientific concepts into simple and clear terms has been so helpful over the years. A great deal of work in this thesis has relied on your knowledge, suggestions, and revisions. It has been a priviledge to have had the opportunity to work and learn from someone as passionate about science as you.

I am fortunate to have collaborated with so many excellent other chemists, materials scientists, engineers, and physicists throughout my PhD work. Without a doubt, Professor David Ginger and his group have had a profound positive influence on my research through extensive collaboration. I'm thankful to Yangwei, Margherita, Fangyuan, Sarthak, Jian, Justin, and others for their help in our collaborations and always patiently answering my elementary questions. I learned so much about lead-halide perovskites, photoluminescence, and materials characterization through our interactions over the years.

I deeply appreciate the support of Professor Juan-Pablo Correa-Baena and his group. Thank you so much for letting me attend your group meetings and always making me feel like I was a part of your group. I'm also thankful to Professor Henry Snaith and his group. I want to thank Joel, Jake, Suer, Ashley, and Benny for their help and support. I also want to thank Professor Joe Berry for his kindness and assistance during my time at NREL. I also appreciate the support of Professor Antoine Kahn and Dr. Dominique Lungwitz. Thank you for collaborating with me and for your helpful insights into the materials systems we studied

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together. Thanks to Professor Carlos Silva-Acuña and Esteban Rojas-Gatjens for their support and generosity over the years. I also want to express my appreciation to Professor Will Gutekunst and Professor Henry LaPierre for their thought comments and feedback on my research.

I want to thank many other members of the Marder group, past and present. I wish to express my deepest gratitude to Dr. Denise Bale for her support. Thank you to Dr. Dan Morton, Dr. Tim Parker, Dr. Yadong Zhang, Dr. Junxiang Zhang, and Dr. Reddy Dasari for always being willing to help and teach me new things in lab. Thank you to Dr. Marie-Hélène Tremblay, Brieuc Le De, Dr. Aiswarya Abhisek Mohapatra and Dr. Khaled Al Kurdi for helping me with my projects in lab and for your friendship. Thanks to Varun, Samik, Cameron, Hye Iang, Victor, Yunping, Patty, Pat, Anirudda, Marvin, Noah, and all my other lab mates for their support and friendship over the years.

Thank you to my funding agencies including the DOE Office of Science Graduate Student Research (SCGSR) Program and the Graduate Assistance in Areas of National Need (GAANN) fellowship.

Thank you to Jay Bolan and Julia Shipman for helping me to sort out so many logistical challenges associated with transferring to CU.

I also wish to express my thanks to the members of my thesis committee, Professor Michael D. McGehee, Professor Oana R. Luca, Professor Jihye Park, and Professor Garry Rumbles. Thank you for your guidance and support.

Finally, I wish to thank my friends and family for all their love and support throughout this journey. Thanks to all my Atlanta friends from the CDC and ALTA tennis teams. Thanks to many great teachers/professors/advisors over the years including Mr. Garst, Mrs. Brinkley, Dr. Leung, Professor Macko, Dr. Chambers, and Dr. Bhandari. Thank you to my brother, Justin, and my sister, Maura, for your support. Thank you to my mother and father, Maureen and William, for always pushing me to succeed and for your eternal support.

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List of Abbreviations

Conduction band		
<i>N</i> , <i>N</i> -Dimethylformamide		
dimethylsulfoxide		
Differential Scanning Calorimetry		
Electron Affinity		
Electron transport layer		
cid		
acid		
C		

PCE	Power conversion efficiency		
p-i-n	positive-intrinsic-negative		
PLQY	Photoluminescence Quantum Yield		
PMMA	Polymethyl methacrylate		
PSC	Perovskite Solar Cell		
QFLS	quasi-Fermi level splitting		
ROMP	Ring Opening Metathesis Polymerization		
SAM	Self-assembled monolayer		
SEM	Scanning electron microscopy		
SKPM	scanning Kelvin-probe microscopy		
Spiro-OMeTAD	2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene		
SRH	Shockley-Read-Hall		
TCO	Transparent conducting oxide		
TCSPC	Time-correlated single photon counting		
TGA	Thermogravimetric Analysis		
ToF-SIMS	Time-of-flight Secondary Ion Mass Spectrometry		
UV-Vis	Ultraviolet-Visible		
VB	Valence band		
Voc	Open-circuit voltage		
XRD	X-ray diffraction		

1 An Overview of Hybrid Metal-Halide Perovskites for Photovoltaics

1.1 Preface: Metal-Halide Perovskites and Renewable Energy

Climate change is perhaps our greatest existential threat. Decarbonizing the economy will be necessary to reduce greenhouse gas emissions. Central to this goal is the need for development and deployment of renewable energy. Of all carbon-neutral sources of energy, sunlight is the largest.¹ The sun provides the earth with ~120,000 TW; If we covered just 0.16% of the Earth's surface with 20% efficient solar panels, we could generate ~38 TW, exceeding projected power needs of ~25 TW in 2040.² A variety of solar cell technologies have been developed; however, thin film metal-halide perovskites represent a promising low cost alternative to existing solar technologies. Metal-halide perovskites possess an unprecedented combination of electronic and optical properties resembling those of traditional inorganic semiconductors yet can be processed at low temperatures from solution. Additionally, these materials have short estimated energy payback times and high potential for integration into tandem-on-silicon solar cells.³ Nevertheless, numerous research challenges remain towards commercialization, including efficiency, stability, scalability and Pb toxicity. Research on perovskite solar cells may allow for improved efficiency and long-term stability of these devices, improving photovoltaic technology and our ability to sustainably source energy.

The conversion of light to electricity has been extensively studied and optimized over the last century. Becquerel first discovered the photovoltaic effect in 1839.⁴ Nearly a century later in 1941, the first silicon solar cell was demonstrated by Ohl at Bell Labs with a power conversion efficiency (PCE) of less than 1%.⁵ Today crystalline silicon solar cells represent the overwhelming majority of photovoltaic market share (>85%) with laboratory modules reaching >25% PCE and commercial modules reaching up to 22%. Various alternatives to first generation

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silicon technologies have been developed within the within the photovoltaic research sector, including so-called second-generation technologies using thin films such as cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS). Finally, third generation photovoltaic technologies consist of emerging technologies such as dye-sensitized, quantum dot, metal-halide perovskite, and organic solar cells.

Amongst emerging photovoltaic technologies, organic-inorganic hybrid perovskites are especially promising and have generated tremendous research interest. Lead-halide perovskites were first reported in photovoltaic devices in 2009 with a PCE of 3.8%.⁶ The latest record single junction perovskite solar cell has reached a certified efficiency of 25.8% and perovskite-silicon tandem solar cells have reached an efficiency of 33.7%.⁷ Their high efficiency, tunable bandgaps (especially for tandems), and ability to leverage years of existing research and materials used in organic and dye sensitized solar cells are a few of the merits of this emerging technology which has led to their use in a variety of optoelectronic devices even beyond solar cells, including light emitting diodes, photodetectors, and x-ray detectors.⁸ The research within this thesis focuses on a materials driven approach to reduce non-radiative losses in perovskite photovoltaics for single junction and tandem-on-silicon applications.

1.2 Semiconductor Physics and Photovoltaics: A Short Overview

Numerous in-depth descriptions of photovoltaic principles exist and as such, only a brief overview will be provided here. Photovoltaic devices operate via the absorption of photons with sufficient energy to generate excited states or excitons (exceeding the threshold photon energy) followed by generation of free carriers. The detailed balance equation, shown below in Equation 1.1, describes the thermodynamic limit of the efficiency of a solar cell based upon the solar

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spectrum, the absorber bandgap, and recombination rate.⁹ The terms are defined below in Table

1.1.

Variable	Definition	Description	Value in detailed balance limit calculation
Xg	$x_g = E_g/kT_s$	The ratio of the bandgap of the absorber, E_g , to the product of the Boltzmann constant, k, and the temperature of the sun, T _s .	
xc	$x_c = T_c/T_s$	The ratio of the temperature of the cell, T_c , to the temperature of the sun, T_s .	
ts	t_s	The probability that a photon with $hv > E_g$ incident on the surface will produce an electron-hole pair.	$t_s = 1$
f	$F_s = A f_{\omega} t_s Q_s$	The total rate of generation of electron-hole pairs from incident solar radiation.	$f = f_{\omega}/2$ (assuming a planar cell radiating from both sides)

$$\eta(x_g, x_c, t_s, f) = \frac{I[V(max)]V(max)}{P_{inc}} = t_s u(x_g) v(f, x_c, x_g) m\left(\frac{vx_g}{x_c}\right)$$
 Equation 1.1

Table 1.1: Variables in the detailed balance equation, their calculation, a brief description and their assumed value in the detailed balance limit.

The parameters $u(x_g)$, $v(x_g, x_c, f)$, and $m(vx_g/x_c)$ are the ultimate efficiency factor, the ratio of the open-circuit voltage or V_{oc} to the bandgap of the cell, E_g, and the impedance matching factor which is a function of the ratio of the V_{oc} to thermal voltage for the cell, respectively. The ultimate efficiency factor accounts for spectrum losses for a given absorber bandgap (where energy from above bandgap photons is lost to thermalization and sub-bandgap photons cannot be collected to generate electron-hole pairs). The impedance matching factor describes the fill factor (FF), or the ratio of the maximum power from the solar cell to the product of the V_{OC} and short circuit current, I_{sc} . Simply put, the maximum power point, or MPT, occurs where the IV product is largest.

A critical assumption in the detailed balance limit is that all photogenerated carriers recombine radiatively. In practice, non-radiative recombination can severely limit the efficiency of the solar cell. Mechanisms of recombination will be thoroughly discussed in the following sections as the reduction of non-radiative recombination in perovskites is a central theme of this thesis.

1.2.1 Overview of Inorganic and Organic Semiconductors

Extensive discussions of fundamental concepts in semiconductors can be found throughout the literature: vacuum level, band structure, conduction and valence bands, Fermi levels, work function, electron affinity, ionization energy, carrier mobility, and conductivity. As such I refer the reader to the following references:

- 1. Kittel, C., Introduction to Solid State Physics. John Wiley & Sons, Inc: 2005.
- Mott, N. F.; Davis, E. A., *Electronic Processes in Non-Crystalline Materials*. Oxford University Press: 2012.
- 3. Brédas, J.-L.; Marder, S. R., *The WSPC Reference on Organic Electronics: Organic Semiconductors*. World Scientific: 2016; Vol. 1.
- 4. Kahn, A., Fermi level, work function and vacuum level. *Materials Horizons* **2016**, *3* (1), 7-10.
- 5. Bredas, J.-L., Mind the gap! *Materials Horizons* **2014**, *1* (1), 17-19.
- 6. Karl, N., Charge carrier transport in organic semiconductors. *Synth. Met.* **2003**, *133-134*, 649-657.
- 7. Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L., Charge Transport in Organic Semiconductors. *Chem. Rev.* **2007**, *107* (4), 926-952.

8. Cahen, D.; Kahn, A., Electron Energetics at Surfaces and Interfaces: Concepts and Experiments. *Adv. Mater.* **2003**, *15* (4), 271-277.

1.2.2 Carrier Generation and Recombination

1.2.2.1 Carrier Generation

Carrier generation takes place via a series of steps. When the energy of an impinging photon equals or exceeds the bandgap of the absorber an electron can be excited from the valence band into the conduction band of the material. This creates an excited state or exciton (a coulombically bound hole-electron pair) which then can dissociate to generate free carriers. In materials with a high dielectric constant, as is the case for many inorganic materials such as silicon, cadmium telluride, and perovskites, Wannier-Mott excitons are formed, which extend over a large range within the lattice, and are weakly bound relative to free charges (with binding energies on the order of 10s of meV) and so can rapidly dissociate to form these free carriers because of electric field screening. On the other hand, Frenkel excitons form within organic semiconductors (as in the case of organic solar cells), where the dielectric constant is low and therefore the exciton binding energy is large (often 100s of meV). There are various approaches towards the optimization of carrier generation including reducing reflection losses and parasitic absorption at the transparent electrode and charge-transport layers (caused in part by differences in the refractive indices of these materials and the absorber layer).¹⁰



Figure 1.1: Plot of energy vs. crystal momentum (k) illustrating the difference between direct (left) and indirect (right) bandgap materials.

The nature of the bandgap of the absorber material has an important consequence on the absorption and thickness of the device. An ideal material would exhibit a large absorption coefficient and long carrier diffusion lengths. Direct bandgap materials, or materials where the conduction band minimal-energy state and the valence band maximal-energy state coincide with respect to the crystal momentum (k-vector), exhibit much stronger optical transitions and therefore only require thin films of the absorber (hundreds of nanometers thick in the case of perovskites). On the other hand, indirect bandgap materials, or materials where the conduction band minimal-energy state and the valence band maximal-energy state do not coincide with respect to the crystal momentum (k-vector), exhibit weaker absorption and require thicker

absorber layers (hundreds of microns thick in the case of Si). The thickness of the material must be counterbalanced by the carrier diffusion lengths. In the case of silicon, minority carrier diffusion lengths are sufficiently large (100s of μ m) to tolerate a relatively large device thickness. In perovskites, carrier diffusion lengths often exceed a micron, which is much longer than the thickness of the absorber layer.¹¹ The subsequent section will briefly discuss the interplay between recombination and the carrier diffusion length.

1.2.2.2 Carrier Recombination

Efficient management of carrier recombination is amongst the most important aspects of achieving an efficient solar cell. Electrons in the conduction band can recombine with holes in the valence band via several different processes. There are three major types of recombination in semiconductors: radiative recombination, Auger recombination, and trap-assisted or Shockley–Read–Hall (SRH) recombination (Figure 1.2).



Figure 1.2: Recombination mechanisms in solar cells. Reproduced from Satpathy and Pamuru with permission.¹²

1.2.2.2.1 Band-to-band Radiative Recombination

Radiative recombination occurs when an electron from the conduction band recombines with a hole from the valence band and emits a photon. Perhaps counterintuitively, a reciprocity relation exists such that a good solar cell must also be a good light emitting diode (LED). The radiative emission of photons is an essential process towards equilibrium and does not constitute energy loss.¹³ As such, radiative recombination should be maximized and will occur to large extent in direct bandgap semiconductors. The relationship between the open-circuit voltage (V_{OC}) of a solar cell and the external luminescence quantum efficiency, EQE_{EL}, is defined from the reciprocity relationship below (Equation 1.2).⁹

$$V_{OC}^{cell} = V_{OC}^{rad} - \frac{kT}{q} |\ln(EQE_{EL})|$$
 Equation 1.2

The open-circuit voltage of the cell, V_{OC}^{cell} , is equal to radiative limit open-circuit voltage, V_{OC}^{rad} , minus the product of the thermal voltage at the operating temperature, kT/q, and the natural logarithm of the electroluminescence external quantum efficiency of the cell operating as a light emitting diode (LED). Thus, to approach the maximum V_{OC}, a material must exhibit near unity external luminescence.

A related quantity is the quasi-Fermi level splitting (QFLS), which is a measure of the difference between the electron quasi-Fermi level, or $E_{F,e}$, and the hole quasi-Fermi level, or $E_{F,h}$. The quasi-Fermi levels are useful to describe the populations of the conduction and valence band under non-equilibrium conditions, such as upon photoexcitation.¹⁴ The precise positions of the quasi-Fermi levels are difficult to measure, however the photoluminescence quantum yield (PLQY) can be used to estimate QFLS by a closely related expression (Equation 1.3).

$$QFLS = QFLS_{rad} - k_BT |\ln(PLQY)|$$
 Equation 1.3

Notably, the internal QFLS is not always equal to the energy equivalent to the external V_{OC} ; the latter can be smaller for a variety of reasons including voltage loss due to misaligned contacts or the introduction of different non-radiative recombination pathways.¹⁵ Furthermore, any process which reduces radiative recombination will reduce the lifetime of charge carriers, the V_{OC} , and

the efficiency of the cell.¹⁶ Lastly, it is noteworthy that radiative recombination can be further beneficial in that an emitted photon can be reabsorbed in a process called "photon recycling" which can enable longer length scales for transport through multiple recombination-emission events.¹⁷

1.2.2.2.2 Auger recombination

Auger recombination occurs when a third carrier interacts with an electron and hole such that the electron and hole recombine, and an electron is promoted to a higher energy level. This results in the promoted electron relaxing via a phonon to the conduction band. This is a type of non-radiative recombination loss, which can occur in some solar cells, especially when the carrier concentration is high.¹²

1.2.2.2.3 Shockley-Read-Hall recombination

The presence of traps enables the conversion of energy to phonons. Traps can occur in the bulk or on the surface of a material because of imperfections in the material such as dangling bonds or impurities. These defects or imperfections create energy states within the bandgap of the material which enable non-radiative loss. These defects occur more prominently at the surfaces or grain boundaries of materials. As discussed in the radiative recombination section, non-radiative recombination via this mechanism heavily influences the quasi-Fermi level splitting and the V_{OC} .¹⁶

1.2.2.2.4 Surface recombination velocity (SRV)

Lastly, a measure of the recombination rate at surfaces is called the surface recombination velocity, S, in units of cm/sec. It occurs from the drift or diffusion of electrons or holes towards recombination centers at the surface.¹⁸ At a surface with no recombination, carriers do not move towards the surface and the surface recombination velocity is 0 cm/sec. At a surface with infinite

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recombination, the surface recombination is limited by the maximum carrier velocity.

Decreasing the rate of depletion of carriers will increase the carrier lifetime and efficiency of the cell.¹⁹

1.3 Hybrid Organic Inorganic Perovskites

There are many relevant reviews covering the optoelectronic properties of lead-halide

perovskites. The following section only intends to briefly introduce these materials in the context

of this thesis and to motivate the research directions undertaken. I refer the reader to any of the

excellent reviews below.

- 1. Green, M. A.; Ho-Baillie, A.; Snaith, H. J., The emergence of perovskite solar cells. *Nat. Photonics* **2014**, *8* (7), 506-514.
- 2. Mitzi, D. B., Introduction: Perovskites. Chem. Rev. 2019, 119 (5), 3033-3035.
- 3. Jena, A. K.; Kulkarni, A.; Miyasaka, T., Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chem. Rev.* **2019**, *119* (5), 3036-3103.
- 4. Kim, J. Y.; Lee, J.-W.; Jung, H. S.; Shin, H.; Park, N.-G., High-Efficiency Perovskite Solar Cells. *Chem. Rev.* **2020**, *120* (15), 7867-7918.
- 5. Lin, X.; Cui, D.; Luo, X.; Zhang, C.; Han, Q.; Wang, Y.; Han, L., Efficiency progress of inverted perovskite solar cells. *Energy Environ. Sci.* **2020**, *13* (11), 3823-3847.
- 6. Snaith, H. J., Present status and future prospects of perovskite photovoltaics. *Nat. Mater.* **2018**, *17* (5), 372-376.
- Correa-Baena, J.-P.; Saliba, M.; Buonassisi, T.; Grätzel, M.; Abate, A.; Tress, W.; Hagfeldt, A., Promises and challenges of perovskite solar cells. *Science* 2017, *358* (6364), 739-744.
- 8. Stoumpos, C. C.; Kanatzidis, M. G., The Renaissance of Halide Perovskites and Their Evolution as Emerging Semiconductors. *Acc. Chem. Res.* **2015**, *48* (10), 2791-2802.
- 9. Park, N.-G., Perovskite solar cells: an emerging photovoltaic technology. *Mater. Today* **2015**, *18* (2), 65-72.
- Correa-Baena, J.-P.; Abate, A.; Saliba, M.; Tress, W.; Jesper Jacobsson, T.; Grätzel, M.; Hagfeldt, A., The rapid evolution of highly efficient perovskite solar cells. *Energy Environ. Sci.* 2017, 10 (3), 710-727.

1.3.1 Perovskite Crystal Structures

Perovskite refers to calcium titanate (CaTiO₃), a mineral named after Russian mineralogist Count Lev A. Perovskiy.⁸ This term has commonly been used to refer to a larger class of compounds with formula ABX₃ and a crystal structure that is the same as, or similar to, that of calcium titanate; the crystal structure consists of octahedrally coordinated B site cations, corner sharing X site anions, and A site cations situated within the cuboctahedral cavities.²⁰ Halide perovskites are the primary materials of interest for solar applications and usually consist of methylammonium (MA⁺), formamidinium (FA⁺), and/or cesium (Cs⁺) as A site cations; lead (Pb²⁺), or tin (Sn²⁺) as B site cations; and iodide (Γ), bromide (Br⁻), and/or chloride (Cl⁻) occupying the X sites.



Figure 1.3: An idealized illustration of a cubic perovskite structure of methylammonium lead iodide (MAPbI₃). The methylammonium cation is surrounded by 12 iodides within the cuboctahedral cavity while the lead dications (gray) exhibit 6-fold coordination to the halide ions (blue). Note that MAPbI₃ exists as a tetragonal phase, which is a lower symmetry structure closely related to this cubic structure, at room temperature.

A simple expression has been developed to help determine the possible constituent anions and cations for the formation of three-dimensional perovskites. The Goldschmidt tolerance factor (Equation 1.3) can be determined from the ionic radii to rationalize the structures formed with various cations and anions, where r_A , r_B , and r_X are the ionic radii of the A-site, B-site, and X-site atoms, respectively.²¹⁻²²

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_x + r_b)}$$
 Equation 1.3

Three-dimensional halide perovskites are typically formed values of *t* between 0.8 and 1.0; values for CsPbI₃, MAPbI₃, and FAPbI₃ increase from 0.81 to 0.91 to 0.98, respectively.²³⁻²⁴

The structure can deform from cubic to tetragonal or orthorhombic with varying anion and cation size and with changes in temperature. MAPbI₃ forms a stable and photoactive tetragonal phase at room temperature but exhibits an orthorhombic to tetragonal phase transition at 162 K and a tetragonal to cubic phase transition at 327 K.²⁵⁻²⁶ FAPbI₃ can form either the black photoactive orthorhombic perovskite phase (α -FAPbI₃) or the yellow hexagonal non-perovskite phase (δ -FAPbI₃), where formation of α -FAPbI₃ typically relies upon annealing at temperatures greater than 150 °C. Humid, ambient air can induce the degradation of α -FAPbI₃ to δ -FAPbI₃.²⁷ Lastly, CsPbI₃ can adopt four distinct polymorphs where most relevant phases are the photoactive α -phase commonly applied in solar cells which can degrade to the non-photoactive δ -phase.²⁸



Figure 1.4: Example structures of (A) 3D, (B) 2D, and (C) 1D perovskites. Representation of (D) vertex-sharing, (E) edge-sharing, and (F) face-sharing 1D perovskite structures. Reproduced from Tremblay et al. with permission.²⁹

Whilst most perovskite research for solar applications has focused on three-dimensional (3D) perovskites, it should also be noted that other hybrid metal-halide compositions can form structures with reduced dimensionality of the metal-halide sublattice; these include two dimensional (2D) perovskites and one dimensional (1D) perovskites, as well as structures that cannot be regarded as being derived from the perovskite structure. Lower dimensional perovskites are generally less suitable for photovoltaics on their own due to their wider bandgaps, but 2D lead-halide perovskites (LHPs) have successfully been used in conjunction with bulk 3D structures to produce very efficient solar cells.³⁰⁻³¹ Two dimensional perovskites consist of sheets of corner-sharing PbX₆ octahedra separated by layers of larger organic cations (generally described by the formula A₂BX₄ or A'BX₄, where A is a monovalent cation and A' is a divalent cation). One-dimensional perovskites can exist in varying stoichiometries depending upon the connectivity of the PbX₆ octahedra (vertex- *vs.* edge- *vs.* face sharing octahedra). Low

dimensional perovskites have concomitant, but at this time less thoroughly understood stereochemical rules, determining their growth.³²

1.3.2 Optoelectronic Properties of Lead-Halide Perovskites

Halide perovskites possess numerous advantageous optoelectronic properties for a variety of device applications, especially solar cells. Hybrid organic-inorganic perovskites (HOIPs) exhibit strong optical absorption and are direct bandgap semiconductors.³³ 3D perovskites exhibit low exciton binding energies (as a consequence of their high dielectric constant) allowing for the generation of free carriers under illumination at room temperature.³⁴ Additionally, 3D perovskites exhibit long hole and electron diffusion lengths and high hole and electron mobilities.^{11, 35}

The position of the valence and conduction bands of lead-halide perovskites is mostly determined by the orbital overlap between the metal and halide ions, whilst the A site cation more minimally affects the band structure as a result of steric and coulombic interactions.³⁶ A useful model is the case of the zero dimensional (PbI₆)⁴⁻ ion, where the highest occupied molecular orbital (HOMO) is formed primarily from overlap of the Pb 6s–I 5p σ -antibonding orbitals and the lowest unoccupied molecular orbital (LUMO) is formed from both from the Pb 6p–I 5p π -antibonding and Pb 6p–I 5s σ -antibonding orbitals. The HOMO and LUMO in (PbI₆)⁴⁻ are ultimately the basis for the valence band and conduction bands in three dimensional halide perovskite material, respectively.³⁷⁻³⁸

As such, the bandgap of perovskites can be tuned by modifying or alloying the halide composition, the A site cation, or the divalent metal (by using other metals like Sn^{2+}).³⁹ Within an analogous series of congeners the bandgap trend for halides is I < Br < Cl, mostly resulting from changes to the valence band position. These changes of the band positions can be visualized

in the energy level diagram derived from a combination of photoelectron spectroscopy data and optical data (Figure 1.5).⁴⁰ Finally, reduction in the dimensionality typically also increases the bandgap.⁴¹



Figure 1.5: Energy level diagram of the various primary ABX₃ 3D metal halide perovskites. Adapted from Tao et al. with permission.⁴⁰

1.3.3 Device Structures and Processing Methods

The structure of perovskite solar cells has evolved considerably since their introduction through an increased understanding of the perovskite absorber properties and a variety of device engineering approaches. The first cells utilized nanocrystalline particles of MAPbI₃ and MAPbBr₃ as sensitizers on a framework of microporous titania—where the perovskite functioned to absorb light and produce excitons and the bulk metal-oxide was used for charge transport.⁶ Later, Lee et al. reported cells which replaced the mesoporous n-type TiO₂ layer with insulating Al₂O₃ as a scaffold atop compact TiO₂ (Figure 1.6 (a)).⁴² This report was groundbreaking in the way that it demonstrated that a sensitization approach was not necessary.⁴³ Another important development was the first highly efficient planar cells (Figure 1.6 (b)). Liu et al. showed that nanostructured layers were not a requirement, which enabled a variety of simplified device architectures.⁴⁴ Several years later, the first efficient inverted (p-i-n) perovskite solar cells were demonstrated by multiple groups.⁴⁵⁻⁴⁷ Inverted cells use a sandwich architecture but unlike "normal" or n-i-p cells, consisted of a hole transport layer atop the bottom (front) transparent electrode and an electron transport layer atop the perovskite at the top (rear) electrode. Today, all the approaches depicted in Figure 1.6 are used, although inverted architectures are perhaps the most promising due to their greater stability and easier integration into tandem on silicon cells.



Figure 1.6: Depiction of the common device structures in perovskite solar cells. (a) n-i-p or regular mesoporous electron transporting layers (represented by network of white circles). (b) Planar n-i-p regular heterojunction approach. (c) Planar p-i-n or inverted structure. Adapted from Lin et al. with permission.⁴⁸

Most perovskite solar cells are fabricated using solution processing. Solution processing can be advantageous for several reasons. Firstly, it should be noted that the highest efficiency perovskite solar cells reported in the open literature have been solution processed.⁴⁹ Additionally, solution processing is considered to be a low-cost fabrication method. An alternative but less commonly used method for processing PSCs is via vacuum deposition. This is advantageous for several reasons. Vacuum deposition is compatible with temperature-sensitive substrates, allows for conformal coatings on non-planar substrates, is solvent-free and allows for straightforward

implementation into tandem solar cells.⁵⁰ Vacuum processing is an established technique in the electronic industry demonstrating high throughput and reliability. Finally, vacuum deposition can enable processing of interfacial materials with limited solubility or solubility not orthogonal to the perovskite layer (sequential deposition).⁵¹

1.3.4 Research Challenges

Research on perovskite solar cells has focused primarily on three areas: efficiency, stability, and scalability. There are many viable research approaches towards one or multiple of these areas, including: active layer (absorber) engineering, modifying existing and developing new transport layers; surface and interface passivation; theoretical and computational modeling; fabrication of flexible or semitransparent devices; lead-sequestration or replacement; and perovskite-perovskite, perovskite-CIGS, and perovskite-silicon tandem cells (of which much of the research focuses on the aforementioned approaches).⁵² Of course, even within these broad areas, there are more specific topics of interest. As this thesis primarily focuses on new electron transport layers and passivation approaches, the remaining section of research challenges will highlight some seminal works and state of the art approaches within these areas.

1.3.4.1 Surface Passivation

An important research area to improve efficiency and stability of perovskite solar cells is surface passivation. Perovskite films contain a high density of defects which can affect charge recombination and ion migration, both critical aspects for high performance and long term stability of devices.⁵³ At the surface or interface of perovskite films, there are discontinuities in the crystal lattice which create defect energy states within the bandgap. Deep traps are states created by charged defects which lie between the valence and conduction bands. These traps increase the rate of nonradiative recombination as described by Shockley–Read–Hall (SRH)

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theory.¹⁶ Shallow traps are considered to have a lesser effect on the rate of non-radiative recombination, however, can result in ion migration under an electric field.⁵³



Figure 1.7: Imperfections in polycrystalline perovskite films and passivation approaches. Adapted from Lin et al. with permission.⁵³

Deep traps decrease the splitting of electron and hole quasi-Fermi levels which lead to a decrease in the open circuit voltage (V_{OC}) of the solar cell. The relationship between V_{OC} and recombination was described previously in the section on band-to-band radiative recombination in Equation 1.2. Recall that the external electroluminescence quantum efficiency (EQE_{EL}) was demonstrated to be a major limiting factor in the solar cell device performance.¹⁶ Thus, a high performance solar cell must also be a highly efficient LED.¹⁶ Most successful passivation molecules suppress non-radiative recombination which is demonstrated by enhanced photoluminescence intensity and lifetime, along with enhancements in PCE mostly as a result of large increases in the V_{oc} .⁵³



Figure 1.8: Calculated transition energy levels for various defects within MAPbI₃. (a) intrinsic acceptors. (b) intrinsic donors. Gray boundaries indicate the relative positions of the valence and conduction bands. The point defects included represent vacancies (V_{MA}, V_{Pb} and V_I), interstitials (MA_i, Pb_i and I_i), and substitutions (MA_{Pb}, Pb_{MA}, MA_I, Pb_I, I_{MA}, and I_{Pb}). Reproduced from Yin et al. with permission.⁵⁴

Perovskite films have several types of defects which increase the rate of nonradiative recombination. They fall into several major categories which include: intrinsic point defects, impurities, two-dimensional extended defects (including grain boundaries), and threedimensional defects such as lead clusters.⁵³ Most defects at the surface are a result of undercoordinated halide ions (X⁻) and lead (Pb²⁺) ions. The energies of various defects and their location relative to the bandgap of MAPbI₃ from first principles calculations are shown in figure 1.8.⁵⁴ Successful passivation of undercoordinated ions has been accomplished both via coordination and ionic bonding.⁵³ Additionally, passivation approaches vary in that molecules can either be added to the perovskite precursor solution or deposited via spin coating atop a perovskite film.⁵⁵

Passivation by coordination of Lewis acids and Lewis bases is a widely utilized approach. Lewis basic molecules, which are thought to coordinate to undercoordinated Pb ions, include thiophene, pyridine, benzylamine, and trioctyl phosphine oxide (TOPO).⁵⁶⁻⁵⁸ It should be noted, however, that primary or secondary amines may react with formamidinium in certain perovskite inks.⁵⁹⁻⁶⁰ Some examples of Lewis acidic molecules include fullerenes and iodopentafluorobenzene. Iodopentafluorobenzene is thought to act as a halogen bond donors



Figure 1.9: Examples of Lewis base passivators (blue) and halogen bond passivator (red). From left to right: thiophene, pyridine, trioctylphosphine oxide (TOPO), and pentafluoroiodobenzene. capable of passivating undercoordinated halogen anions, whereas fullerenes may either coordinate to undercoordinated halide ions or coordinate Pb–I antisite defects (PbI₃⁻).^{53, 57, 61-62} Ionic passivation interactions are another approach towards the passivation of perovskites. Various alkali metal halide salts as well as some transition metal halide salts have produced very high efficiencies.⁵³ Two especially noteworthy examples include incorporation of potassium iodide and incorporation of rubidium iodide.⁶³⁻⁶⁴ Many organic ammonium iodide salts have been used as passivation agents including phenylethylammonium iodide (PEAI) and butylammonium iodide.⁶⁵⁻⁶⁶ It should also be note that these ammonium salts can induce the formation of wide bandgap layered phases when added to the precursor solution.⁶⁷⁻⁶⁸ Another approach which falls within this category is the use of zwitterionic passivation agents. A *tert*-butyl-phenylalanine derivative was found to be very effective in reducing non-radiative recombination and thus increasing open circuit voltage (V_{oc}).⁵⁵

Numerous surface passivation agents have been identified and have produced very high device efficiencies in the literature.^{55, 57, 69} However, several challenges remain. Firstly, some passivation agents are extremely effective for increasing the photoluminescence quantum yield (PLQY) of films but are insulating and cannot be implemented in devices.⁷⁰ Furthermore, many candidate passivation molecules are not commercially available and thus this has limited the chemical space of what has been explored so far. The synthesis of new molecules may aid in the identification of new passivation agents and in identification of the precise mode(s) of chemical interaction. Finally, the precise chemical nature of the interaction of the passivation molecule with the traps is difficult to elucidate. Various passivation treatments may work well for a specific perovskite composition but few "universal" passivation agents have been identified, especially for methylammonium-free compositions.⁷¹

1.3.4.2 Electron Transport Materials

PSCs incorporate charge-carrier transport layers that are used between the perovskite absorbing layer and charge collecting electrodes. These layers are used to selectively transport a charge carrier (either holes or electrons) to the appropriate electrode.⁷² Electron transporting materials (ETMs) for PSCs should have good energy alignment with the perovskite layer and a high electron (n-type) mobility. Not only should the LUMO of the ETM align closely with the conduction band of the perovskite, but also the HOMO of the ETM should function to block hole transport as a result of poor energy alignment (lower HOMO energy) with the valence band of the perovskite.⁷³ Additionally, these materials should be soluble in a solvent that does not dissolve the perovskite layer (when deposited by solution processing), provide uniform film coverage, and act to passivate defects in the perovskite layer.⁷² Ideal charge transport layers should not contribute to non-radiative losses when in contact with the perovskite.⁷⁴ In certain

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device architectures (like n-i-p in single junction cells and in tandem solar cells) it is critical that charge extraction layers have minimal absorption in the visible region to reduce parasitic absorption.⁷⁵

A variety of inorganic and organic electron transport layers have been explored for use in perovskite solar cells. To date, TiO₂ is the most widely used electron transport material in PSCs—owing at least in part to its widespread use in dye-sensitized solar cells (DSSCs).⁷⁶ TiO₂ possesses good conduction band alignment (-4.1 eV) for commonly used perovskites such as the triple cation (CsMAFA) perovskite (4.0 eV)⁷⁷ and relatively good electron mobility (0.1-4 cm² V⁻¹ s⁻¹).⁷⁸ In spite of this, there are some disadvantages including its UV light instability, photocatalytic properties, and generally high sintering temperatures (>450 °C,⁷⁹ although novel processing techniques have been used to enable fabrication of TiO₂ ETMs at lower temperatures⁸⁰⁻⁸¹). SnO₂ represents an excellent alternative material which has been widely implemented in highly efficient cells.⁴⁹ Tin (IV) oxide exhibits good energy alignment and high electron mobility (exceeding 400 cm² V⁻¹ s⁻¹).⁸² SnO₂ layers can be processed by spin coating and chemical bath deposition at lower temperatures.⁸³ Another less widely used ETL is ZnO, which can be fabricated via low-temperature solution processes; however, perovskites atop ZnO exhibit low thermal stability and so far devices have yielded more modest efficiencies.⁸⁴ Alternative metal oxides and sulfides such as CdS,⁸⁵ BaSnO₃,⁸⁶ Nb₂O₅,⁸⁷ and SrTiO₃⁸⁸ have also recently been explored as alternatives.⁸⁹

Devices utilizing organic semiconductors as interfacial layers in PSCs possess some advantages over their inorganic counterparts. Specifically, the optoelectronic properties are more easily adjusted through structural modifications, device processing is easier, batches are more reproducible, and flexible devices can be produced when fabricated on certain substrates,

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improving versatility.⁷²⁻⁷³ These organic semiconductors are typically either small molecules or polymers. Small molecules provide certain advantages over polymers in that they are monodisperse, synthesized reliably and reproducibly, and have adjustable structure-packing features. On the other hand, polymeric materials can be advantageous as ETMs due to enhanced control of morphology and improved compatibility with other layers.⁷³ Furthermore, polymeric materials may be crosslinked to impart solvent resistance to allow subsequent solution processing of other layers, and, in some cases, to improve stability to moisture and/or immobilize dopant ions.^{73, 75}

Of the existing organic semiconductor ETMs, fullerenes have been used as and have produced relatively efficient devices in p-i-n architectures. Fullerenes offer good charge transporting properties and have been reported to passivate the perovskite surface,⁵³ but exhibit poor solubility and lack long term stability.⁹⁰ The perovskite/C₆₀ interface represents a substantial source of non-radiative losses within inverted perovskite solar cells.⁹¹⁻⁹² Thus, identifying new electron transport layers may help to overcome these interfacial losses. Alternative ETMs that are more transparent might offer improved performance, decreased interfacial losses, and better device stability. Furthermore, solution processable polymeric and crosslinkable materials may increase processing flexibility.

Rylene diimides, widely explored for the fabrication of n-channel organic field-effect transistors (OFETs), are a family of molecules with favorable energy alignment and electron transport properties.⁹³ Perylene diimides (PDIs) have been explored as electron transport materials as small molecules (including related dimers



Figure 1.10: PDI dimer reported by Cheng and coworkers

and other derivatives). Cheng and coworkers developed a high efficiency (PCE of 17.1%) p-i-n device with the PDI dimer shown in figure 1.10. Their ETM exhibited a mobility similar to PCBM, but offered improved stability when stored in humid, dark and atmospheric conditions for 15 days.⁷² A polymeric PDI, naphthodiperylenetetraimide-vinylene-based polymer (NDP-V), was implemented in a n-i-p device. The material exhibited higher mobility than PCBM as well as improved device efficiency relative to the PCBM reference device (16.5% vs 15.3%).⁹⁴

Naphthalene diimides as ETMs in PSCs have produced some of the highest device efficiencies of all nonfullerene ETMs. Naphthalene diimides (NDIs), like PDIs, are relatively easily synthesized and are highly soluble in many organic solvents.⁷² Only a limited number of groups have investigated this motif for PSCs. Of all small molecule NDIs



Figure 1.11: Homochiral NDI reported by Kwon and coworkers.

used in perovskite solar cells, the homochiral NDI-PhE molecule shown in Figure 1.11 has produced the most efficient devices. Kwon and co-workers reported an efficiency of 20.5% in a p-i-n device where the modified structure improved 3-D isotropic electron transport properties relative to their previously reported bis-1-indanyl functionalized NDI.^{72, 95-96} NDI polymers, in spite of good LUMO alignment, have demonstrated lower PCE relative to their small molecule counterparts. One of the most efficient devices was fabricated using PFN-Ox-doped N2200. The doped device showed improved efficiency (16.8%) relative to the undoped device (15.0%).⁹⁷

Azaacenes are a class of molecules which may be synthesized rather easily and are highly soluble in solvents favorable for solution processing, like dichlorobenzene. Several groups have reported azaacenes used in p-i-n devices with efficiencies exceeding 18%.^{90, 98} Wang et al. reported a HATNT derivative (Figure 1.12) and attributed performance improvements to improved mobility and suppressed non-



Figure 1.4: HATNT reported by Wang and coworkers.

radiative recombination relative to a PCBM control device. Lastly, several other non-fullerene small molecules for electron transport which don't fit into the above categories have been used in perovskite solar cells. Indaceno-based molecular ETMs used in PSCs have demonstrated efficiencies of up to 19.5% with a high V_{oc} of 1.11 V.⁷³

There are several examples of fullerene-based crosslinkable ETMs, specifically utilizing silanes and benzocyclobutenes as crosslinkable groups.⁹⁹⁻¹⁰⁰ To my knowledge, few others have explored crosslinkable non-fullerene small molecules and polymers as ETMs. Zhu et al. reported a HATNA small molecule derivative functionalized with three methacrylate groups which could be crosslinked via thiol-ene reaction thermally at ~110 °C. Undoped devices had a relatively low PCE of 12.0% but upon doping device performance was improved with a PCE of 18.2%. In the same work, they also report an "all-crosslinked" device (where both the ETM and HTM were crosslinked) with a PCE of 16.1%. Both devices showed improved stability relative to a PCBM reference device in ambient conditions.¹⁰¹ On the other hand, crosslinkable hole transport materials (HTMs) have been more extensively explored in the literature with a variety of crosslinking methods including thiol-ene reaction as well as incorporation of styrene analogues, benzophenones and cinnamates as crosslinking groups/methods.^{75, 102-103}

In addition to pointing out a lack of crosslinkable ETMs, it is also necessary to point out that the majority of the non-fullerene ETMs reported use p-i-n (inverted) device architectures, where the transparency of the ETM is of little relevance. Thus, many of these materials may be less suitable for n-i-p devices as well as tandem devices (especially p-i-n tandems). New research should focus on identifying existing and synthesizing new molecules with a higher optical transparency in the visible region to reduce parasitic absorption and enable versatility in their device applications.

1.4 General Overview and Organization of Thesis

This thesis addresses several current issues relevant to PSCs. Chapter 2 describes the synthesis, characterization, and material properties of an NDI side chain copolymer incorporating cinnamate crosslinking groups. We demonstrate the polymer's high transparency, thermal stability, photocrosslinking, and n-doping via solution and sequential processes. Finally, we demonstrate its applicability in PSCs through characterization of solar-cell device performance relative to its uncrosslinked homopolymeric counterpart in n-i-p devices with a MA-free perovskite absorber.

In chapter 3, a large photoluminescence-based screening of passivation materials is described. Candidate passivators were screened across a variety of perovskite compositions. A benzylammonium trifluoromethanesulfonate salt, BAOTf, was identified as a highly effective passivation molecule, allowing for the fabrication of solar cells exhibiting very low hysteresis with PCEs >19% with a MA-free mixed-cation mixed-halide perovskite absorber (Cs17Br25).

In chapter 4, the reactivity of amines and ammoniums with formamidinium salts was explored. Understanding solution reactivity of amines with formamidinium salts enabled the synthesis, isolation, and implementation of the product(s) formed in these reactions as additives

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and surface passivation agents in perovskites. This work helped to elucidate the role of the amine/ammonium additives in controlling FA-containing perovskite growth and crystallization processes.

In chapter 5, I discuss the limitations of this research and offer some potential new research directions. I describe possible approaches for the development of new non-fullerene electron transport materials, methodology for screening passivation agents to mitigate interfacial losses, and the potential to further elucidate the role of formamidinium adducts in lead-halide perovskite inks and films.

References:

1. Lewis, N. S.; Crabtree, G.; Nozik, A. J.; Wasielewski, M. R.; Alivisatos, P.; Kung, H.; Tsao, J.; Chandler, E.; Walukiewicz, W.; Spitler, M.; Ellingson, R.; Overend, R.; Mazer, J.; Gress, M.; Horwitz, J.; Ashton, C.; Herndon, B.; Shapard, L.; Nault, R. M. *Basic Research Needs for Solar Energy Utilization*; April 18-21, 2005, 2005.

2. *International Energy Outlook 2018 (IEO2018)*; U.S. Energy Information Administration: 2018.

3. Wang, M.; Shi, Z.; Fei, C.; Deng, Z. J. D.; Yang, G.; Dunfield, S. P.; Fenning, D. P.; Huang, J., Ammonium cations with high pKa in perovskite solar cells for improved high-temperature photostability. *Nat. Energy* **2023**.

4. Becquerel M, E., Memoire sur les Effets Electriques Produits sous l'Influence des Rayons Solaires. *Comptes Rendus Hebdomadaires des Seances de L'Academie des Sciences* **1839**, *9*, 561-567.

5. Green, M. A., The path to 25% silicon solar cell efficiency: History of silicon cell evolution. *Progress in Photovoltaics: Research and Applications* **2009**, *17* (3), 183-189.

6. Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T., Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131* (17), 6050-6051.

7. NREL. Best Research-Cell Efficiency Chart. <u>https://www.nrel.gov/pv/cell-efficiency.html</u> (accessed 19 October 2022).

8. Jena, A. K.; Kulkarni, A.; Miyasaka, T., Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chem. Rev.* **2019**, *119* (5), 3036-3103.

9. Shockley, W.; Queisser, H. J., Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *J. Appl. Phys.* **2004**, *32* (3), 510-519.

10. Luo, D.; Su, R.; Zhang, W.; Gong, Q.; Zhu, R., Minimizing non-radiative recombination losses in perovskite solar cells. *Nature Reviews Materials* **2020**, *5* (1), 44-60.

11. Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J., Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* **2013**, *342* (6156), 341-344.

12. Satpathy, R.; Pamuru, V., Chapter 4 - Making of crystalline silicon solar cells. In *Solar PV Power*, Satpathy, R.; Pamuru, V., Eds. Academic Press: 2021; pp 71-134.

13. Miller, O. D.; Yablonovitch, E.; Kurtz, S. R., Strong Internal and External Luminescence as Solar Cells Approach the Shockley–Queisser Limit. *IEEE Journal of Photovoltaics* **2012**, *2* (3), 303-311.

14. Shockley, W., The Theory of p-n Junctions in Semiconductors and p-n Junction Transistors. *Bell System Technical Journal* **1949**, *28* (3), 435-489.

15. Caprioglio, P.; Stolterfoht, M.; Wolff, C. M.; Unold, T.; Rech, B.; Albrecht, S.; Neher, D., On the Relation between the Open-Circuit Voltage and Quasi-Fermi Level Splitting in Efficient Perovskite Solar Cells. *Adv. Energy Mater.* **2019**, *9* (33), 1901631.

16. Tress, W., Perovskite Solar Cells on the Way to Their Radiative Efficiency Limit -Insights Into a Success Story of High Open-Circuit Voltage and Low Recombination. *Adv. Energy Mater.* **2017**, *7* (14).

17. Pazos-Outón, L. M.; Szumilo, M.; Lamboll, R.; Richter, J. M.; Crespo-Quesada, M.; Abdi-Jalebi, M.; Beeson, H. J.; Vrućinić, M.; Alsari, M.; Snaith, H. J.; Ehrler, B.; Friend, R. H.; Deschler, F., Photon recycling in lead iodide perovskite solar cells. *Science* **2016**, *351* (6280), 1430-1433.

18. Sproul, A. B., Dimensionless solution of the equation describing the effect of surface recombination on carrier decay in semiconductors. *J. Appl. Phys.* **1994**, *76* (5), 2851-2854.

Weiss, T. P.; Bissig, B.; Feurer, T.; Carron, R.; Buecheler, S.; Tiwari, A. N., Bulk and surface recombination properties in thin film semiconductors with different surface treatments from time-resolved photoluminescence measurements. *Scientific Reports* **2019**, *9* (1), 5385.
 Green, M. A.; Ho-Baillie, A.; Snaith, H. J., The emergence of perovskite solar cells.

Nature Photonics **2014**, 8 (7), 506-514.

Pazoki, M.; Edvinsson, T., Metal replacement in perovskite solar cell materials: chemical bonding effects and optoelectronic properties. *Sustainable Energy Fuels* 2018, 2 (7), 1430-1445.
 Goldschmidt, V. M., Die Gesetze der Krystallochemie. *Naturwissenschaften* 1926, 14 (21), 477-485.

Kieslich, G.; Sun, S.; Cheetham, A. K., Solid-state principles applied to organic– inorganic perovskites: new tricks for an old dog. *Chemical Science* 2014, 5 (12), 4712-4715.
Liu, D.; Zha, W.; Guo, Y.; Sa, R., Insight into the Improved Phase Stability of CsPbI3

from First-Principles Calculations. ACS Omega **2020**, 5 (1), 893-896.

25. Quarti, C.; Mosconi, E.; Ball, J. M.; D'Innocenzo, V.; Tao, C.; Pathak, S.; Snaith, H. J.; Petrozza, A.; De Angelis, F., Structural and optical properties of methylammonium lead iodide across the tetragonal to cubic phase transition: implications for perovskite solar cells. *Energy & Environmental Science* **2016**, *9* (1), 155-163.

26. Bonadio, A.; Sabino, F. P.; Freitas, A. L. M.; Felez, M. R.; Dalpian, G. M.; Souza, J. A., Comparing the Cubic and Tetragonal Phases of MAPbI3 at Room Temperature. *Inorg. Chem.* **2023**, *62* (19), 7533-7544.

27. Ma, F.; Li, J.; Li, W.; Lin, N.; Wang, L.; Qiao, J., Stable α/δ phase junction of formamidinium lead iodide perovskites for enhanced near-infrared emission. *Chemical Science* **2017**, 8 (1), 800-805.

28. Montecucco, R.; Quadrivi, E.; Po, R.; Grancini, G., All-Inorganic Cesium-Based Hybrid Perovskites for Efficient and Stable Solar Cells and Modules. *Adv. Energy Mater.* **2021**, *11* (23), 2100672.

29. Tremblay, M.-H.; Boyington, A.; Rigin, S.; Jiang, J.; Bacsa, J.; Al Kurdi, K.; Khrustalev, V. N.; Pachter, R.; Timofeeva, T. V.; Jui, N.; Barlow, S.; Marder, S. R., Hybrid Organic Lead Iodides: Role of Organic Cation Structure in Obtaining 1D Chains of Face-Sharing Octahedra vs 2D Perovskites. *Chem. Mater.* **2022**, *34* (3), 935-946.

30. Metcalf, I.; Sidhik, S.; Zhang, H.; Agrawal, A.; Persaud, J.; Hou, J.; Even, J.; Mohite, A. D., Synergy of 3D and 2D Perovskites for Durable, Efficient Solar Cells and Beyond. *Chem. Rev.* **2023**, *123* (15), 9565-9652.

31. Proppe, A. H.; Johnston, A.; Teale, S.; Mahata, A.; Quintero-Bermudez, R.; Jung, E. H.; Grater, L.; Cui, T.; Filleter, T.; Kim, C.-Y.; Kelley, S. O.; De Angelis, F.; Sargent, E. H., Multication perovskite 2D/3D interfaces form via progressive dimensional reduction. *Nature Communications* **2021**, *12* (1), 3472.

32. Mao, L.; Stoumpos, C. C.; Kanatzidis, M. G., Two-Dimensional Hybrid Halide Perovskites: Principles and Promises. *J. Am. Chem. Soc.* **2019**, *141* (3), 1171-1190.

33. Sarritzu, V.; Sestu, N.; Marongiu, D.; Chang, X.; Wang, Q.; Masi, S.; Colella, S.; Rizzo, A.; Gocalinska, A.; Pelucchi, E.; Mercuri, M. L.; Quochi, F.; Saba, M.; Mura, A.; Bongiovanni,

G., Direct or Indirect Bandgap in Hybrid Lead Halide Perovskites? *Advanced Optical Materials* **2018**, *6* (10), 1701254.

34. Miyata, A.; Mitioglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J., Direct measurement of the exciton binding energy and effective masses for charge carriers in organic–inorganic tri-halide perovskites. *Nature Physics* **2015**, *11* (7), 582-587.

35. Herz, L. M., Charge-Carrier Mobilities in Metal Halide Perovskites: Fundamental Mechanisms and Limits. *ACS Energy Letters* **2017**, *2* (7), 1539-1548.

36. Stoumpos, C. C.; Kanatzidis, M. G., The Renaissance of Halide Perovskites and Their Evolution as Emerging Semiconductors. *Acc. Chem. Res.* **2015**, *48* (10), 2791-2802.

37. Elumalai, N. K.; Mahmud, M. A.; Wang, D.; Uddin, A. Perovskite Solar Cells: Progress and Advancements *Energies* [Online], 2016.

38. Umebayashi, T.; Asai, K.; Kondo, T.; Nakao, A., Electronic structures of lead iodide based low-dimensional crystals. *Physical Review B* **2003**, *67* (15), 155405.

39. Xiao, Z.; Zhou, Y.; Hosono, H.; Kamiya, T.; Padture, N. P., Bandgap Optimization of Perovskite Semiconductors for Photovoltaic Applications. *Chemistry – A European Journal* **2018**, *24* (10), 2305-2316.

40. Tao, S.; Schmidt, I.; Brocks, G.; Jiang, J.; Tranca, I.; Meerholz, K.; Olthof, S., Absolute energy level positions in tin- and lead-based halide perovskites. *Nature Communications* **2019**, *10* (1), 2560.

41. Manser, J. S.; Christians, J. A.; Kamat, P. V., Intriguing Optoelectronic Properties of Metal Halide Perovskites. *Chem. Rev.* **2016**, *116* (21), 12956-13008.

42. Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J., Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science* **2012**, *338* (6107), 643-647.

43. Park, N.-G., Perovskite solar cells: an emerging photovoltaic technology. *Mater. Today* **2015,** *18* (2), 65-72.

44. Liu, M.; Johnston, M. B.; Snaith, H. J., Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* **2013**, *501* (7467), 395-398.

45. Roldán-Carmona, C.; Malinkiewicz, O.; Betancur, R.; Longo, G.; Momblona, C.; Jaramillo, F.; Camacho, L.; Bolink, H. J., High efficiency single-junction semitransparent perovskite solar cells. *Energy & Environmental Science* **2014**, *7* (9), 2968-2973.

46. Seo, J.; Park, S.; Chan Kim, Y.; Jeon, N. J.; Noh, J. H.; Yoon, S. C.; Seok, S. I., Benefits of very thin PCBM and LiF layers for solution-processed p–i–n perovskite solar cells. *Energy & Environmental Science* **2014**, *7* (8), 2642-2646.

47. Nie, W.; Tsai, H.; Asadpour, R.; Blancon, J.-C.; Neukirch, A. J.; Gupta, G.; Crochet, J. J.; Chhowalla, M.; Tretiak, S.; Alam, M. A.; Wang, H.-L.; Mohite, A. D., High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science* **2015**, *347* (6221), 522-525.

48. Lin, X.; Cui, D.; Luo, X.; Zhang, C.; Han, Q.; Wang, Y.; Han, L., Efficiency progress of inverted perovskite solar cells. *Energy & Environmental Science* **2020**, *13* (11), 3823-3847.

49. Yoo, J. J.; Seo, G.; Chua, M. R.; Park, T. G.; Lu, Y.; Rotermund, F.; Kim, Y.-K.; Moon, C. S.; Jeon, N. J.; Correa-Baena, J.-P.; Bulović, V.; Shin, S. S.; Bawendi, M. G.; Seo, J., Efficient perovskite solar cells via improved carrier management. *Nature* **2021**, *590* (7847), 587-

593.

50. Yuan, Q.; Lohmann, K. B.; Oliver, R. D. J.; Ramadan, A. J.; Yan, S.; Ball, J. M.; Christoforo, M. G.; Noel, N. K.; Snaith, H. J.; Herz, L. M.; Johnston, M. B., Thermally Stable

Perovskite Solar Cells by All-Vacuum Deposition. *ACS Applied Materials & Interfaces* **2023**, *15* (1), 772-781.

51. Momblona, C.; Gil-Escrig, L.; Bandiello, E.; Hutter, E. M.; Sessolo, M.; Lederer, K.; Blochwitz-Nimoth, J.; Bolink, H. J., Efficient vacuum deposited p-i-n and n-i-p perovskite solar cells employing doped charge transport layers. *Energy Environ. Sci.* **2016**, *9* (11), 3456-3463.

52. Shikoh, A. S.; Polyakov, A., A Quantitative Analysis of the Research Trends in Perovskite Solar Cells in 2009–2019. *physica status solidi (a)* **2020**, *217* (23), 2000441.

53. Chen, B.; Rudd, P. N.; Yang, S.; Yuan, Y.; Huang, J., Imperfections and their passivation in halide perovskite solar cells. *Chem. Soc. Rev.* **2019**, *48* (14), 3842-3867.

54. Yin, W.-J.; Shi, T.; Yan, Y., Unusual defect physics in CH3NH3PbI3 perovskite solar cell absorber. *Appl. Phys. Lett.* **2014**, *104* (6), 063903.

55. Yang, S.; Dai, J.; Yu, Z.; Shao, Y.; Zhou, Y.; Xiao, X.; Zeng, X. C.; Huang, J., Tailoring Passivation Molecular Structures for Extremely Small Open-Circuit Voltage Loss in Perovskite Solar Cells. *J. Am. Chem. Soc.* **2019**, *141* (14), 5781-5787.

56. Noel, N. K.; Abate, A.; Stranks, S. D.; Parrott, E. S.; Burlakov, V. M.; Goriely, A.; Snaith, H. J., Enhanced Photoluminescence and Solar Cell Performance via Lewis Base Passivation of Organic–Inorganic Lead Halide Perovskites. *ACS Nano* **2014**, *8* (10), 9815-9821.

57. Wang, F.; Geng, W.; Zhou, Y.; Fang, H.-H.; Tong, C.-J.; Loi, M. A.; Liu, L.-M.; Zhao, N., Phenylalkylamine Passivation of Organolead Halide Perovskites Enabling High-Efficiency and Air-Stable Photovoltaic Cells. *Adv. Mater.* **2016**, *28* (45), 9986-9992.

58. Palazon, F.; Pérez-del-Rey, D.; Marras, S.; Prato, M.; Sessolo, M.; Bolink, H. J.; Manna, L., Coating Evaporated MAPI Thin Films with Organic Molecules: Improved Stability at High Temperature and Implementation in High-Efficiency Solar Cells. *ACS Energy Letters* **2018**, *3* (4), 835-839.

59. Taddei, M.; Smith, J. A.; Gallant, B. M.; Zhou, S.; Westbrook, R. J. E.; Shi, Y.; Wang, J.; Drysdale, J. N.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Snaith, H. J.; Ginger, D. S., Ethylenediamine Addition Improves Performance and Suppresses Phase Instabilities in Mixed-Halide Perovskites. *ACS Energy Letters* **2022**, 4265-4273.

60. Jiang, Q.; Tong, J.; Xian, Y.; Kerner, R. A.; Dunfield, S. P.; Xiao, C.; Scheidt, R. A.; Kuciauskas, D.; Wang, X.; Hautzinger, M. P.; Tirawat, R.; Beard, M. C.; Fenning, D. P.; Berry, J. J.; Larson, B. W.; Yan, Y.; Zhu, K., Surface reaction for efficient and stable inverted perovskite solar cells. *Nature* **2022**, *611* (7935), 278-283.

61. Abate, A.; Saliba, M.; Hollman, D. J.; Stranks, S. D.; Wojciechowski, K.; Avolio, R.; Grancini, G.; Petrozza, A.; Snaith, H. J., Supramolecular Halogen Bond Passivation of Organic– Inorganic Halide Perovskite Solar Cells. *Nano Lett.* **2014**, *14* (6), 3247-3254.

62. Shao, Y.; Xiao, Z.; Bi, C.; Yuan, Y.; Huang, J., Origin and elimination of photocurrent hysteresis by fullerene passivation in CH3NH3PbI3 planar heterojunction solar cells. *Nature Communications* **2014**, *5* (1), 5784.

63. Abdi-Jalebi, M.; Andaji-Garmaroudi, Z.; Cacovich, S.; Stavrakas, C.; Philippe, B.; Richter, J. M.; Alsari, M.; Booker, E. P.; Hutter, E. M.; Pearson, A. J.; Lilliu, S.; Savenije, T. J.; Rensmo, H.; Divitini, G.; Ducati, C.; Friend, R. H.; Stranks, S. D., Maximizing and stabilizing luminescence from halide perovskites with potassium passivation. *Nature* **2018**, *555* (7697), 497-501.

64. Zhang, M.; Yun, J. S.; Ma, Q.; Zheng, J.; Lau, C. F. J.; Deng, X.; Kim, J.; Kim, D.; Seidel, J.; Green, M. A.; Huang, S.; Ho-Baillie, A. W. Y., High-Efficiency Rubidium-

Incorporated Perovskite Solar Cells by Gas Quenching. ACS Energy Letters 2017, 2 (2), 438-444.

65. Jokar, E.; Chien, C.-H.; Fathi, A.; Rameez, M.; Chang, Y.-H.; Diau, E. W.-G., Slow surface passivation and crystal relaxation with additives to improve device performance and durability for tin-based perovskite solar cells. *Energy & Environmental Science* **2018**, *11* (9), 2353-2362.

66. Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J., Surface passivation of perovskite film for efficient solar cells. *Nature Photonics* **2019**, *13* (7), 460-466.

67. Wang, Z.; Lin, Q.; Chmiel, F. P.; Sakai, N.; Herz, L. M.; Snaith, H. J., Efficient ambientair-stable solar cells with 2D–3D heterostructured butylammonium-caesium-formamidinium lead halide perovskites. *Nature Energy* **2017**, *2* (9), 17135.

68. Hu, Y.; Schlipf, J.; Wussler, M.; Petrus, M. L.; Jaegermann, W.; Bein, T.; Müller-Buschbaum, P.; Docampo, P., Hybrid Perovskite/Perovskite Heterojunction Solar Cells. *ACS Nano* **2016**, *10* (6), 5999-6007.

69. Shi, Y.; Rojas-Gatjens, E.; Wang, J.; Pothoof, J.; Giridharagopal, R.; Ho, K.; Jiang, F.; Taddei, M.; Yang, Z.; Sanehira, E. M.; Irwin, M. D.; Silva-Acuña, C.; Ginger, D. S., (3-Aminopropyl)trimethoxysilane Surface Passivation Improves Perovskite Solar Cell Performance by Reducing Surface Recombination Velocity. *ACS Energy Letters* **2022**, *7* (11), 4081-4088.

70. deQuilettes, D. W.; Koch, S.; Burke, S.; Paranji, R. K.; Shropshire, A. J.; Ziffer, M. E.;
Ginger, D. S., Photoluminescence Lifetimes Exceeding 8 μs and Quantum Yields Exceeding
30% in Hybrid Perovskite Thin Films by Ligand Passivation. ACS Energy Letters 2016, 1 (2),
438-444.

71. Jariwala, S.; Burke, S.; Dunfield, S.; Shallcross, R. C.; Taddei, M.; Wang, J.; Eperon, G. E.; Armstrong, N. R.; Berry, J. J.; Ginger, D. S., Reducing Surface Recombination Velocity of Methylammonium-Free Mixed-Cation Mixed-Halide Perovskites via Surface Passivation. *Chem. Mater.* **2021**, *33* (13), 5035-5044.

72. Said, A. A.; Xie, J.; Zhang, Q., Recent Progress in Organic Electron Transport Materials in Inverted Perovskite Solar Cells. *Small* **2019**, *15* (27), e1900854.

73. Lian, J.; Lu, B.; Niu, F.; Zeng, P.; Zhan, X., Electron-Transport Materials in Perovskite Solar Cells. *Small Methods* **2018**, *2* (10).

74. Wang, J.; Fu, W.; Jariwala, S.; Sinha, I.; Jen, A. K. Y.; Ginger, D. S., Reducing Surface Recombination Velocities at the Electrical Contacts Will Improve Perovskite Photovoltaics. *ACS Energy Letters* **2019**, *4* (1), 222-227.

75. Tremblay, M.-H.; Schutt, K.; Zhang, Y.; Lim, J.; Lin, Y.-H.; Warby, J. H.; Barlow, S.; Snaith, H. J.; Marder, S. R., A photo-crosslinkable bis-triarylamine side-chain polymer as a hole-transport material for stable perovskite solar cells. *Sustainable Energy Fuels* **2020**, *4* (1), 190-198.

76. Wang, J.; Liu, Y.; Chen, X.; Chen, C.; Chen, P.; Wang, Z.; Duan, Y., Functional Metal Oxides in Perovskite Solar Cells. *ChemPhysChem* **2019**, *20* (20), 2580-2586.

Al-Ashouri, A.; Magomedov, A.; Roß, M.; Jošt, M.; Talaikis, M.; Chistiakova, G.;
Bertram, T.; Márquez, J. A.; Köhnen, E.; Kasparavičius, E.; Levcenco, S.; Gil-Escrig, L.; Hages, C. J.; Schlatmann, R.; Rech, B.; Malinauskas, T.; Unold, T.; Kaufmann, C. A.; Korte, L.; Niaura, G.; Getautis, V.; Albrecht, S., Conformal monolayer contacts with lossless interfaces for perovskite single junction and monolithic tandem solar cells. *Energy & Environmental Science* 2019, *12* (11), 3356-3369.

78. Cao, Z.; Li, C.; Deng, X.; Wang, S.; Yuan, Y.; Chen, Y.; Wang, Z.; Liu, Y.; Ding, L.; Hao, F., Metal oxide alternatives for efficient electron transport in perovskite solar cells: beyond TiO2 and SnO2. *Journal of Materials Chemistry A* **2020**, *8* (38), 19768-19787.

79. Smith, J. A.; Game, O. S.; Bishop, J. E.; Spooner, E. L. K.; Kilbride, R. C.; Greenland, C.; Jayaprakash, R.; Alanazi, T. I.; Cassella, E. J.; Tejada, A.; Chistiakova, G.; Wong-Stringer, M.; Routledge, T. J.; Parnell, A. J.; Hammond, D. B.; Lidzey, D. G., Rapid Scalable Processing of Tin Oxide Transport Layers for Perovskite Solar Cells. *ACS Applied Energy Materials* **2020**, *3* (6), 5552-5562.

80. Ranjan, S.; Ranjan, R.; Tyagi, A.; Rana, K. S.; Soni, A.; Kodali, H. K.; Dalal, V.; Singh, A.; Garg, A.; Nalwa, K. S.; Gupta, R. K., Low-Temperature Microwave Processed TiO2 as an Electron Transport Layer for Enhanced Performance and Atmospheric Stability in Planar Perovskite Solar Cells. *ACS Applied Energy Materials* **2022**, *5* (3), 2679-2696.

81. Wang, J. T.-W.; Ball, J. M.; Barea, E. M.; Abate, A.; Alexander-Webber, J. A.; Huang, J.; Saliba, M.; Mora-Sero, I.; Bisquert, J.; Snaith, H. J.; Nicholas, R. J., Low-Temperature Processed Electron Collection Layers of Graphene/TiO2 Nanocomposites in Thin Film Perovskite Solar Cells. *Nano Lett.* **2014**, *14* (2), 724-730.

82. Ke, W.; Zhao, D.; Cimaroli, A. J.; Grice, C. R.; Qin, P.; Liu, Q.; Xiong, L.; Yan, Y.; Fang, G., Effects of annealing temperature of tin oxide electron selective layers on the performance of perovskite solar cells. *Journal of Materials Chemistry A* **2015**, *3* (47), 24163-24168.

83. Wu, P.; Wang, S.; Li, X.; Zhang, F., Advances in SnO2-based perovskite solar cells: from preparation to photovoltaic applications. *Journal of Materials Chemistry A* **2021**, *9* (35), 19554-19588.

84. Luo, J.; Wang, Y.; Zhang, Q., Progress in perovskite solar cells based on ZnO nanostructures. *Solar Energy* **2018**, *163*, 289-306.

85. Liu, J.; Gao, C.; Luo, L.; Ye, Q.; He, X.; Ouyang, L.; Guo, X.; Zhuang, D.; Liao, C.; Mei, J.; Lau, W., Low-temperature, solution processed metal sulfide as an electron transport layer for efficient planar perovskite solar cells. *Journal of Materials Chemistry A* **2015**, *3* (22), 11750-11755.

86. Zhu, L.; Shao, Z.; Ye, J.; Zhang, X.; Pan, X.; Dai, S., Mesoporous BaSnO3 layer based perovskite solar cells. *Chem. Commun.* **2016**, *52* (5), 970-973.

87. Ling, X.; Yuan, J.; Liu, D.; Wang, Y.; Zhang, Y.; Chen, S.; Wu, H.; Jin, F.; Wu, F.; Shi, G.; Tang, X.; Zheng, J.; Liu, S.; Liu, Z.; Ma, W., Room-Temperature Processed Nb2O5 as the Electron-Transporting Layer for Efficient Planar Perovskite Solar Cells. *ACS Applied Materials & Interfaces* **2017**, *9* (27), 23181-23188.

88. Neophytou, M.; De Bastiani, M.; Gasparini, N.; Aydin, E.; Ugur, E.; Seitkhan, A.; Moruzzi, F.; Choaie, Y.; Ramadan, A. J.; Troughton, J. R.; Hallani, R.; Savva, A.; Tsetseris, L.; Inal, S.; Baran, D.; Laquai, F.; Anthopoulos, T. D.; Snaith, H. J.; De Wolf, S.; McCulloch, I., Enhancing the Charge Extraction and Stability of Perovskite Solar Cells Using Strontium Titanate (SrTiO3) Electron Transport Layer. *ACS Applied Energy Materials* **2019**, *2* (11), 8090-8097.

89. Lin, L.; Jones, T. W.; Yang, T. C.-J.; Duffy, N. W.; Li, J.; Zhao, L.; Chi, B.; Wang, X.; Wilson, G. J., Inorganic Electron Transport Materials in Perovskite Solar Cells. *Adv. Funct. Mater.* **2021**, *31* (5), 2008300.

90. Jung, S. K.; Lee, D. S.; Ann, M. H.; Im, S. H.; Kim, J. H.; Kwon, O. P., Non-Fullerene Organic Electron-Transporting Materials for Perovskite Solar Cells. *ChemSusChem* **2018**, *11* (22), 3882-3892.

91. Stolterfoht, M.; Wolff, C. M.; Márquez, J. A.; Zhang, S.; Hages, C. J.; Rothhardt, D.; Albrecht, S.; Burn, P. L.; Meredith, P.; Unold, T.; Neher, D., Visualization and suppression of interfacial recombination for high-efficiency large-area pin perovskite solar cells. *Nature Energy* **2018**, *3* (10), 847-854.

92. Warby, J.; Zu, F.; Zeiske, S.; Gutierrez-Partida, E.; Frohloff, L.; Kahmann, S.; Frohna, K.; Mosconi, E.; Radicchi, E.; Lang, F.; Shah, S.; Peña-Camargo, F.; Hempel, H.; Unold, T.; Koch, N.; Armin, A.; De Angelis, F.; Stranks, S. D.; Neher, D.; Stolterfoht, M., Understanding Performance Limiting Interfacial Recombination in pin Perovskite Solar Cells. *Adv. Energy Mater.* **2022**, *12* (12), 2103567.

93. Quinn, J. T. E.; Zhu, J.; Li, X.; Wang, J.; Li, Y., Recent progress in the development of ntype organic semiconductors for organic field effect transistors. *Journal of Materials Chemistry C* 2017, 5 (34), 8654-8681.

94. Jiang, K.; Wu, F.; Zhu, L.; Yan, H., Naphthodiperylenetetraimide-Based Polymer as Electron-Transporting Material for Efficient Inverted Perovskite Solar Cells. *ACS Applied Materials & Interfaces* **2018**, *10* (42), 36549-36555.

95. Jung, S. K.; Heo, J. H.; Lee, D. W.; Lee, S. H.; Lee, S. C.; Yoon, W.; Yun, H.; Kim, D.; Kim, J. H.; Im, S. H.; Kwon, O. P., Homochiral Asymmetric-Shaped Electron-Transporting Materials for Efficient Non-Fullerene Perovskite Solar Cells. *ChemSusChem* **2019**, *12* (1), 224-230.

96. Jung, S.-K.; Heo, J. H.; Lee, D. W.; Lee, S.-C.; Lee, S.-H.; Yoon, W.; Yun, H.; Im, S. H.; Kim, J. H.; Kwon, O. P., Nonfullerene Electron Transporting Material Based on Naphthalene Diimide Small Molecule for Highly Stable Perovskite Solar Cells with Efficiency Exceeding 20%. *Adv. Funct. Mater.* **2018**, *28* (20).

97. Zhu, Z.; Chueh, C.-C.; Zhang, G.; Huang, F.; Yan, H.; Jen, A. K. Y., Improved Ambient-Stable Perovskite Solar Cells Enabled by a Hybrid Polymeric Electron-Transporting Layer. *ChemSusChem* **2016**, *9* (18), 2586-2591.

98. Wang, N.; Zhao, K.; Ding, T.; Liu, W.; Ahmed, A. S.; Wang, Z.; Tian, M.; Sun, X. W.; Zhang, Q., Improving Interfacial Charge Recombination in Planar Heterojunction Perovskite Photovoltaics with Small Molecule as Electron Transport Layer. *Adv. Energy Mater.* **2017**, 7 (18).

99. Wojciechowski, K.; Ramirez, I.; Gorisse, T.; Dautel, O.; Dasari, R.; Sakai, N.; Hardigree, J. M.; Song, S.; Marder, S.; Riede, M.; Wantz, G.; Snaith, H. J., Cross-Linkable Fullerene Derivatives for Solution-Processed n–i–p Perovskite Solar Cells. *ACS Energy Letters* 2016, *1* (4), 648-653.

100. Bai, Y.; Dong, Q.; Shao, Y.; Deng, Y.; Wang, Q.; Shen, L.; Wang, D.; Wei, W.; Huang, J., Enhancing stability and efficiency of perovskite solar cells with crosslinkable silane-functionalized and doped fullerene. *Nature Communications* **2016**, *7* (1), 12806.

101. Zhu, Z.; Zhao, D.; Chueh, C.-C.; Shi, X.; Li, Z.; Jen, A. K. Y., Highly Efficient and Stable Perovskite Solar Cells Enabled by All-Crosslinked Charge-Transporting Layers. *Joule* **2018**, *2* (1), 168-183.

102. Zheng, L.; Mukherjee, S.; Wang, K.; Hay, M. E.; Boudouris, B. W.; Gong, X., Radical polymers as interfacial layers in inverted hybrid perovskite solar cells. *Journal of Materials Chemistry A* **2017**, *5* (45), 23831-23839.

103. Xu, J.; Voznyy, O.; Comin, R.; Gong, X.; Walters, G.; Liu, M.; Kanjanaboos, P.; Lan, X.; Sargent, E. H., Crosslinked Remote-Doped Hole-Extracting Contacts Enhance Stability under Accelerated Lifetime Testing in Perovskite Solar Cells. *Adv. Mater.* **2016**, *28* (14), 2807-15.

2 Photo-Crosslinkable Naphthalene Diimide Polymer for Solution-Processed n-i-p Perovskite Solar Cells



Figure 2.1: Graphical abstract depicting the reverse J-V scan of the champion device, the polymer structure, and the device architecture.

This project was a collaboration with Yangwei Shi, Dominique Lungwitz, and Aiswarya Abhisek Mohapatra. Yangwei Shi prepared and optimized photovoltaic devices, Dominique Lungwitz measured the conductivity of the doped polymers, and Aiswarya Abhisek Mohapatra helped to develop the sequential doping protocol. Much of this chapter is adapted from a manuscript (in review) cowritten with Yangwei Shi.

This work was primarily supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technology Office (SETO), Award Number DE-EE0008747. I also wish to acknowledge support of this project by the Department of Education Graduate Assistance in Areas of National Need (GAANN) program at Georgia Institute of Technology (Award #P200A180075).

2.1 Introduction

Hybrid organic-inorganic lead halide perovskite solar cells are a rapidly emerging photovoltaic technology that has reached power conversion efficiencies (PCEs) exceeding 26%.¹ Typically perovskite solar cells incorporate charge-selective transport layers which are used between the perovskite absorber and charge-collecting electrodes. Metal-oxide electron-transport layers (ETLs) have been widely used in n-i-p perovskite solar cells for a variety of reasons including their moderate to high electron mobilities, good energy alignment with the perovskite conduction band, and wide bandgaps that reduce parasitic absorption and offer hole-blocking capability.^{2,3} TiO₂ remains the most common ETL used in state-of-the-art n-i-p cells but requires high processing temperatures and exhibits photo-instability.⁴ A variety of modified processing techniques have been developed to reduce surface defects and to enable processing of TiO2 at lower temperatures.^{5,6,7} Alternatively, SnO₂ has been used due to its better photostability, higher electron mobility, and ability to be processed at lower temperatures.^{8,9} Another less widely used ETL is ZnO which can be fabricated via low-temperature solution processes; however, perovskites atop ZnO exhibit low thermal stability and so far devices have yielded more modest efficiencies.¹⁰ Recently, alternative metal oxides and sulfides such as CdS,¹¹ BaSnO₃,¹² Nb₂O₅,¹³ SrTiO₃,¹⁴ and others have also been explored as alternatives.³

Organic electron transport materials represent another possible alternative to metal oxides. Organic semiconductors offer processing flexibility, tailored energy level alignment, and opportunities to decrease non-radiative recombination losses at the electron-extraction interface.^{15,16} Of the existing organic semiconductor ETLs, fullerenes have been widely adopted and have produced efficient devices in both normal (n-i-p)¹⁷ and more commonly in inverted (p-in) architectures.¹⁸ Fullerenes offer good charge-transport properties but have poor solubility, and suboptimal transparency in the visible. However, fullerenes can be a substantial source of interfacial recombination losses,^{16,19} and devices incorporating fullerenes as ETLs generally lack long term stability.^{20,21} Chemically insolubilized fullerene layers have been utilized by various groups to improve stability and enable solution processing.^{22,23}

Alternative non-fullerene organic ETLs have been employed as small molecules and polymers including perylene diimides,^{24,25} naphthalene diimides,^{26,27,28} and azaacenes.^{29,30} Amongst these candidate classes of materials, naphthalene diimides are particularly attractive as they possess high transparency throughout the visible region, electron affinities comparable with those of perovskites combined with high hole-blocking ionization energies, and in some cases, good electron transport properties.³¹ Furthermore, the synthesis of naphthalene diimides is straightforward and can be readily modified to tune both their solubility and electron affinity via substitution at the imide and naphthalene core positions.³² Naphthalene diimide acceptors have been incorporated in a number of polymeric architectures for various applications in organic electronics,³³ but less widely in perovskite photovoltaics. Hole-transporting polymers such as PTAA,^{34,35} Poly-TPD,³⁶ PEDOT:PSS³⁷ and P3HT³⁸ have been more widely and successfully incorporated as hole-transporting materials in perovskite solar cells, where they can be advantageous over small molecules due to their excellent film-forming properties, enhanced control of morphology, and improved compatibility with other layers.² Furthermore, polymeric materials may be crosslinked to impart solvent resistance, which can allow for subsequent solution processing of other layers, and, in some cases, to improve stability to moisture and/or immobilize dopant ions.^{2,39} Numerous crosslinking approaches have been used for transport layers in the literature;⁴⁰ however, cinnamates represent a particularly attractive approach as the crosslinking

reaction is selective, they are tolerant of molecular redox dopants, and they can be crosslinked via mild photoirradiation.^{39,41,42}

We previously reported the use of a naphthalene diimide side chain homopolymer that achieved stabilized PCEs of >13.5% in n-i-p perovskite solar cells.⁴³ Seeking to improve upon this work, we report here the synthesis, characterization, and material properties of a related new copolymer (NDI-CL) which incorporates cinnamate crosslinking groups. We demonstrate this polymer's high transparency, thermal stability, photo-crosslinking, and n-doping via solution and sequential processing. We demonstrate its applicability in perovskite solar cells through characterization of solar cell device performance relative to its uncrosslinked homopolymeric counterpart (NDI-1) in n-i-p devices with a MA-free perovskite absorber (MA⁺ = methylammonium).

2.2 Experimental

<u>General</u>

All chemicals were purchased from commercial sources and used as received, unless stated otherwise. Column chromatography was carried out using silica gel (46-63 µm, Sorbent) as the stationary phase, and thin-layer chromatography (TLC) was performed on precoated silica-gel plates (0.25 mm thick, 60F254, EMD, Germany) and visualized under UV light. Nuclear magnetic spectroscopy measurements were carried out on Bruker Avance III 400 or Avance III HD 500 MHz instruments and calibrated using the solvent residual as an internal reference (CHCl₃,7.26 ppm ¹H NMR, 77.16 ppm ¹³C NMR). Polymers were analyzed using a Tosoh EcoSEC HLC 8320 GPC system equipped with a TSKgel SuperHZ-L column with CHCl₃ eluant containing 0.25% NEt₃ at a flow rate of 0.45 mL/min at 40 °C. All number-average molecular weights and dispersities were calculated from refractive index chromatograms using PStQuick Mp-M

polystyrene standards. Elemental analyses were carried out by Atlantic Microlabs using a LECO 932 CHNS elemental analyzer.

Materials and methods

All precursors were used without further purification and were stored in a nitrogen-filled glovebox. Formamidinium iodide (FAI, Greatcell), cesium iodide (CsI, Sigma), lead iodide (PbI₂, Sigma) and lead bromide (PbBr₂, Sigma) were dissolved in a mixture of anhydrous *N*,*N*-dimethylformamide (DMF, Sigma) and anhydrous dimethyl sulfoxide (DMSO, Sigma) (volume ratio of 4:1) to prepare a 1.2 M solution of FA_{0.83}Cs_{0.17}Pb(I_{0.75}Br_{0.15})₃ according to the stoichiometry.

Patterned indium tin oxide (ITO, from thin film devices) glass substrates and glass substrates were cleaned by sequentially sonicating in water containing ~2% Micro-90 detergent, DI water, acetone, and isopropanol (IPA) for 10 min, respectively, followed by plasma-cleaning for 5 min. The perovskite precursor solution was filtered through a PTFE filter before use and 50 μ L of the solution was deposited on top of the substrate and spin-coated at 4000 rpm for 60 s. When ~35 s remained, 120 μ L anhydrous chlorobenzene (CB, Sigma) antisolvent was dropped from the top. The perovskite films were then annealed at 100 °C for 30 s and 150 °C for 10 min.¹ The preparation of perovskite films was carried out in a nitrogen-filled glovebox.

Films for crosslinking and contact angle measurements

To prepare films of NDI-CL, NDI-CL was dissolved in anhydrous chlorobenzene (10 mg/mL). 100 μ L of the resultant solution was deposited statically and spin coated at 1000 rpm for 60s atop 1 in x 1 in O₃ cleaned glass substrates (ITO substrates in the case of contact angle measurements). The films were annealed for 10 min at 100°C. The films were crosslinked using an Analytik-Jena compact UV lamp (UVGL-25) at 365 nm for 20 min.

Solar cell fabrication

To fabricate the Cs17Br15 devices, NDI-1and NDI-CL were dissolved in anhydrous chlorobenzene (CB) with a concentration of 1 mg/mL. 60 μ L of the solution was deposited onto the ITO substrate before spin-coating at 3000 rpm for 30 s. NDI-CL was then irradiated under UV (UVGL-25 Compact UV Lamp) light at 365 nm (~5 cm above the film) for 20 min to crosslink the polymer. The Al₂O₃ (Sigma) was diluted in isopropyl alcohol (IPA) with a volume ratio of 1:150, which was spin coated at 3000 rpm for 30 s, followed by annealing at 100 °C for ~1 min. The perovskite films were deposited in the same way as mentioned above. Spiro-OMeTAD (Xi'an Polymer light technology Corp.) was used as the hole transport layer. The HTL solution was prepared by dissolving 60 mg of Spiro-OMeTAD in 700 μ L CB, with addition of 22.5 μ L 4-*tert*-butylpyridine (t-BP, Sigma-Aldrich) and 15.5 μ L of Li-TFSI solution (520 mg/mL in acetonitrile, ACN, Sigma-Aldrich). The 60 μ L HTL solution was spin coated on top of perovskite at 3000 rpm for 30s in a nitrogen-filled glovebox. Subsequently, the half stack solar cell devices were stored in a desiccator for 24 h. To complete the device fabrication, 80 nm Au was thermally evaporated onto the devices.

Solar cell characterization

Current-voltage (*J-V*) characteristics under 1 Sun equivalent illumination were measured using an ORIEL LSH-7320 ABA LED solar simulator in a nitrogen-filled glovebox, which is calibrated with a filtered KG3 Silicon reference solar cell certified by the National Renewable Energy Laboratory (NREL). The effective area of the solar cell is ~0.0453 cm². *J-V* scans were carried out with a Keithley 2400 controlled by a program written in LabView. The voltage values are scanned at a 0.02 V step in the range of -0.1 V to 1.2 V. The steady-state power output was carried out by measuring the solar cells at maximum power point (MMP) and 1 Sun intensity. The shunt resistances of perovskite solar cells were estimated by following Lee et al.,² using the lumped equivalent circuit model and differentiating the J-V curve to obtain the shunt resistance at short-circuit current.

Drift diffusion simulations by SCAPS

The effect of cathode work function on device performance was studied by simulations with a device structure of ITO/Perovskite/Spiro-OMeTAD/Au shown in Figure 2.13. We varied the work function of cathode from 4.01 eV to 4.51 eV with a step size of 0.1 eV. The surface recombination velocity at both electrodes was fixed at ~ 1000 cm/s. The simulation parameters for perovskite were adopted from Jariwala et al.³ except that the thickness of perovskite layer was set at 500 nm.¹ The parameters of Spiro-OMeTAD were adopted from Bouazizi et al.⁴

X-ray diffraction

A Bruker D8 Powder X-ray diffractometer (XRD) with a high-efficiency Cu anode microfocus Xray source and sensitive Pilatus 100K large-area 2D detector was used to study the crystal information of perovskite films.

UV-vis absorption spectroscopy

UV-vis absorbance spectra of the perovskite films were measured on an Agilent 8453 UV-Vis Spectrometer with wavelength in the range of 200-1100 nm. UV-vis absorbance spectra of the polymers were measured on a Cary 5000 UV-Vis-NIR Spectrophotometer.

Atomic Force Microscopy (AFM)

The AFM images were collected using an Asylum Research MFP3D mounted on an inverted optical microscope with a 75 kHz tip.

Scanning Kelvin probe microscopy (SKPM)

The SKPM images of NDI polymer-modified ITO substrates were measured with an Asylum Research MFP3D mounted on an inverted optical microscope by using 325 kHz tip under dark.

Time-resolved photoluminescence (TRPL)

TRPL was measured by using a PicoQuant Picoharp 300 TCSPC system equipped with a 640 nm pulsed diode laser. The laser was pulsed at repetition rates of 1 MHz, excited from ITO side. The PL emission was filtered using a 700 nm long-pass filter before being directed to the detector. The PL lifetime was fitted by using a stretched exponential decay function as shown in previous work.⁵

PL emission

PL emission (excited at 640 nm) was measured using Edinburgh FLS1000 spectrometer with a Xenon lamp light source. A PMT-980 detector was used for PL measurements.

Scanning electron microscopy (SEM)

SEM images were acquired by using a FEI Sirion SEM at 2 kV accelerating voltage. The sample structure was ITO/NDI/Al₂O₃/perovskite.

Cyclic Voltammetry

Electrochemical measurements were carried out in dry deoxygenated dichloromethane solutions of 0.1 M in tetra-n-butylammonium hexafluorophosphate using a BAS 100 B/W Potentiostat, a glassy carbon working electrode, a platinum auxiliary electrode, and, as a pseudo-reference electrode, a silver wire anodized in 1 M aqueous potassium chloride. Potentials were referenced to ferrocenium / ferrocene by using ferrocene as an internal reference. Cyclic voltammograms were recorded at a scan rate of 100 mVs⁻¹.

Contact Angle Goniometry

Measurements were conducted on a ramé-hart goniometer, using water and diiodomethane as probe liquids (0.2 μ L). A drop (typically two repetitions at different spots on the substrate) was quickly placed on the surface, the needle was pulled back, and the drop shape was captured immediately with the camera. Measurements were collected in triplicate for each drop at an interval of 20 s. Images were analyzed with drop shape analysis software to determine the contact angle by the method most suitable for each given drop, usually height-width, and the results were averaged. The error bars displayed are the calculated uncertainty based on the standard deviation. The displayed images in Figure 2.15 are at t₀.

Thermogravimetric Analysis (TGA)

Measurement was performed on a Mettler Toledo TGA 2 over 30-800 °C, at

20.00 °C/min, and with a N_2 flow rate of 20.0 mL/min.

Differential Scanning Calorimetry (DSC)

Measurement was performed on TA Instruments Q200 Differential Scanning Calorimeter (DSC) with a ramp rate of 10.00 °C/min.

Materials:



Figure 2.2: Structures of organic materials used in this study.

Synthesis:

The NDI monomer, the polymer NDI-1, and cinnamate alcohol were synthesized according to previously reported literature procedures.^{6,7} (N-DMBI)₂ and 4-Bx were also synthesized according to previously reported procedures.^{8,9}

Cinnamate Monomer



Figure 2.3: Synthesis of cinnamate monomer.

3-(4-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenoxy)propyl-bicyclo[2.2.1]hept-5-ene-2-

carboxylate, Cinnamate monomer, was synthesized via a Steglich esterification.³⁹ 1.00 g (4.23 mmol) of cinnamate alcohol and 0.76 g (5.50 mmol) *exo*-5-norbornene-2-carboxylic acid were added to an oven dried 50 mL two neck round-bottomed flask with a stirring bar. The flask was then fitted with a septum, then pumped and refilled with nitrogen 3 times. Then 15 mL of anhydrous dichloromethane (DCM) was added, and the mixture was stirred until dissolution. Then 1.75 g (8.46 mmol) of *N*,*N'*-Dicyclohexylcarbodiimide (DCC) and 0.036 g (0.296 mmol) of 4-dimethylaminopyridine (DMAP) were dissolved in 5 mL of anhydrous DCM. The resulting solution was added dropwise via syringe to the reaction mixture. The reaction was stirred overnight. The solvent was removed under reduced pressure and the resulting mixture was triturated with MeOH. The resulting solid was purified by flash chromatography (80:20 DCM:EA). The collected fractions were concentrated under reduced pressure. The resulting solid

was recrystallized from a mixture of DCM and methanol, filtered, and dried under high vacuum to collect a white solid product (0.917g, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.51 – 7.42 (m, 2H), 6.94 – 6.85 (m, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.17 – 6.06 (m, 2H), 4.29 (t, *J* = 6.2 Hz, 2H), 4.09 (t, *J* = 6.2 Hz, 2H), 3.79 (s, 3H), 3.02 (ddd, *J* = 3.2, 1.6, 0.8 Hz, 1H), 2.91 (s, 1H), 2.27 – 2.18 (m, 1H), 2.14 (quintet, *J* = 6.2 Hz, 2H), 1.91 (dt, *J* = 11.9, 4.0 Hz, 1H), 1.50 (dt, *J* = 8.3, 1.6 Hz, 1H), 1.42 – 1.31 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 176.35, 167.90, 160.71, 144.61, 138.23, 135.81, 129.87, 127.34, 115.46, 114.93, 64.68, 61.24, 51.73, 46.75, 46.48, 43.26, 41.75, 30.48, 28.75. HRMS (ESI) m/z calculated for C₂₁H₂₅O₅ [(M+H)⁺] 357.1697, found 357.1689. Anal. Calcd for C₂₁H₂₅O₅: C, 70.77; H, 6.79; N, 0. Found: C, 70.74; H, 6.65; N, 0.

¹H NMR:



Figure 2.4: ¹H-NMR spectrum of cinnamate monomer in CDCl₃.

¹³C-NMR



Figure 2.5: ¹³C{¹H} NMR spectrum of cinnamate monomer in CDCl₃.

Cinnamate copolymer



Figure 2.6: Synthesis of cinnamate copolymer.

poly-[(5-(7-hexyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1H)yl)pentyl norbornene-2-carboxylate)-*ran*-((E)-3-(4-(3-methoxy-3-oxoprop-1-en-1yl)phenoxy)propyl norbornene-2-carboxylate)], Cinnamate copolymer, was synthesized via a ring opening polymerization (ROMP) with the so-called Grubbs I initiator.^{8, 38} 0.50 g (0.90 mmol) of NDI monomer and 0.137 g (0.385 mmol) of cinnamate monomer were added to an oven dried round-bottomed flask equipped with a stirring bar. The flask was purged and refilled with nitrogen three times. The solids were dissolved in anhydrous DCM (7 mL) under nitrogen. "First generation" Grubbs initiator (10.5 mg, 0.0128 mmol) was added to a separate vial, purged and refilled with nitrogen three times, then dissolved in dichloromethane (1.0 mL). The resulting solution was added to the reaction mixture via syringe. The reaction mixture was stirred overnight. The reaction was quenched by the addition of excess ethyl vinyl ether. The resulting solid was dissolved in dichloromethane and precipitated in MeOH three times and subsequently was isolated by vacuum filtration as a yellow solid (0.542 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ 8.67 (s, 4H), 7.52 (s, 0H), 7.36 (s, 1H), 6.81 (s, 1H), 6.20 (s, 1H), 5.35 (s, 2H), 5.17 (s, 1H), 4.23 (s, 1H), 4.14 (s, 5H), 4.04 (s, 3H), 3.75 (d, *J* = 4.6 Hz, 1H), 3.06 (s, 0H), 2.94 (s, 0H), 2.67 (s, 2H), 2.50 (s, 3H), 2.11 – 2.04 (m, 2H), 1.92 (s, 2H), 1.75 – 1.67 (m, 8H), 1.58 (s, 3H), 1.49 – 1.37 (m, 5H), 1.33 (d, *J* = 14.3 Hz, 1H), 1.33 (s, 3H), 1.16 (s, 1H), 0.92 – 0.84 (m, 3H). Anal. Calcd for [C₃₃H₃₆N₂O₆]_{0.7}[C₂₁H₂₅O₅]_{0.3}: C, 71.07; H, 6.60; N, 3.52. Found: C, 70.53; H, 6.72; N, 3.75. GPC analysis in CHCl₃: M_n = 45.4 kDa, M_w/M_n = 1.17.

¹H NMR







Figure 2.8: Cyclic voltammogram of NDI monomer 0.1 M NBu₄PF₆ in DCM. Referenced to ferrocenium / ferrocene by using ferrocene as an internal reference. $E_{1/2}^{0/-} = 1.10$ V and $E_{1/2}^{-/2-} = 1.50$ V vs. FeCp₂^{0/+}.

2.3 **Results and Discussion**

2.3.1 Polymer Synthesis

Figure 1 shows the polymer structures and their syntheses. The naphthalene diimide monomer (1) and the corresponding homopolymer (NDI-1, see Figure 2.2 for its molecular structure) were synthesized for this work ($M_n = 54.5 \text{ kDa}$, D = 1.50) following methods previously reported.⁴³ The cinnamate norbornene monomer was synthesized over two steps (Figure 2.3): the commercially available methyl 4-hydroxycinnmate (2) was etherified to methyl 4-(3-hydroxypropoxy)cinnamate (3) by deprotonation with anhydrous potassium carbonate and alkylation with 3-bromo-1-propanol in *N*,*N*-dimethylformamide (DMF). The norbornene cinnamate monomer (4) was then synthesized by a Steglich esterification with *exo*-5-norbornenecarboxylic acid using dicyclohexylcarbodiimide (DCC) and catalytic 4-dimethylaminopyridine (DMAP). The polymer (NDI-CL) was synthesized by ring-opening metathesis polymerization (ROMP) of the naphthalene diimide monomer and cinnamate monomer in a 7:3 ratio, respectively, with Grubbs 1st generation catalyst in

dichloromethane (DCM) ($M_n = 45.4$ kDa, $\tilde{D} = 1.17$). The polymer exhibited good solubility in low polarity solvents commonly used in device processing such as chloroform, chlorobenzene, and dichlorobenzene.



Figure 2.9: Synthesis and molecular structure of NDI-1 and cinnamate copolymer (NDI-CL).

2.3.2 Polymer Crosslinking, n-Doping and Thermal Characterization

We characterized the optical properties and crosslinking of thin films of NDI-CL cast from chlorobenzene. The UV-Vis absorption spectrum of NDI-CL prior to crosslinking shows a vibronically structured feature similar to that of small-molecule unsubstituted NDIs (Figure 2.10a),³² with a broad unstructured absorption peaking at *ca*. 310 nm attributable to the absorption of the *para*-alkoxy-substituted cinnamate moiety.⁴¹ We then photo-irradiated the films at 365 nm with a handheld UV lamp for 25 minutes; the observed changes in the absorption spectrum over time – the absorbance of the cinnamate feature decreases to reach a near minimum after *ca*. 20 minutes irradiation (Figure 2.10a) – we attribute to the [2 + 2] cycloaddition reaction of the cinnamate. Subsequently in Figure 2.11 we demonstrate the solvent resistance of the films towards both the casting solvent and the perovskite ink solvent mixture, chlorobenzene and 4:1 DMF:DMSO (DMSO = dimethyl sulfoxide), respectively, by spin coating each solvent atop the crosslinked films and showing negligible changes in the absorption spectrum.



Figure 2.10 (a) UV-vis absorption spectrum of NDI-CL film on glass with increasing irradiation time with 365 nm handheld UV lamp. (b) Conductivity of solution and sequentially doped NDI-1 and NDI-CL films, LOD represents limit of detection. (c) Thermogravimetric analysis (TGA) of NDI-CL polymer and derivative weight. (d) Differential scanning calorimetry of NDI-CL polymer.



Figure 2.11: (a) Solvent resistance of photo-crosslinked film towards polymer casting solvent, chlorobenzene (CB). (b) Solvent resistance of photo-crosslinked film towards perovskite casting solvent, volume ratio 4:1 of DMF:DMSO.

Once we had established an effective crosslinking protocol, we sought to investigate the charge-transport properties of these materials. In the absence of doping, the conductivities were below the limit of detection (<10⁻¹⁰ S/cm) of our apparatus. We used the highly reducing but moderately air-stable dimeric benzimidazole dopant, (N-DMBI)₂, as a reducing agent.⁴⁴ Solution doping was carried out on NDI-1 (9 mol % dimeric dopant) without the addition of a crosslinker. Solution doping of the copolymer (9 mol % dimeric dopant) was followed by crosslinking. We
also investigated a sequential doping protocol where a dopant solution (6 mg/mL) was applied to the crosslinked film followed by chlorobenzene washing step. For sequential doping, NDI-1 was crosslinked by 5% weight addition of an oligomeric azide crosslinker, 4Bx, shown in Figure 2.2 followed by photoirradiation at 254 nm for 5 minutes.⁴⁵ Figure 2.10b shows that all polymer dopant systems exhibit modest conductivities $(10^{-9}-10^{-6} \text{ S/cm})$. Additionally, solution-doped NDI-1 exhibited better conductivity by several orders of magnitude compared to the solution-doped and crosslinked NDI-CL. Sequentially-doped and crosslinked NDI-CL had slightly better conductivity than its solution-doped and crosslinked counterpart, perhaps because the polymer morphology was less interrupted by the doping process. In summary, doping of these side chain naphthalene diimide polymers improves their conductivity, but only achieving values of $10^{-9}-10^{-6}$ S/cm, which is less than other state-of-the-art n-doped electron-transporting polymers, which can reach conductivities of 1.1×10^{-3} S/cm.⁴⁶

We also characterized the thermal properties of NDI-CL (without photo-crosslinking) by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), shown in Figure 2c and 2d, respectively. The TGA indicates the decomposition temperature of the polymer, T_d, defined as temperature at which 5% of mass is lost, is *ca.* 335 °C. The first DSC cycle shows a small endotherm around 80 °C which likely reflects loss of trapped solvent (note in Figure S6 trace of DCM present according to ¹HNMR spectroscopy). Additionally, a melting peak is observed around 135 °C in the first cycle. However, after the thermal history of the polymer has been cleared, we observe no transitions up to 200 °C in the second cycle. The excellent thermal stability of the polymer implies compatibility with high temperature annealing steps for the deposition of other layers in perovskite solar cell devices.

2.3.3 Workfunction of Polymer Thin-Films



Figure 2.12: SKPM surface potential images of (a) NDI-1 and (b) NDI-CL modified ITO substrates. Scale bar in both images is $1 \mu m$.

We dissolved NDI-1 and NDI-CL in anhydrous chlorobenzene to form solutions with a concentration of 1 mg/mL prior to spin-coating onto ITO substrates. The thickness of the NDI polymer films was estimated to be ~ 4 nm using atomic force microscopy (AFM) measurements (Figure 2.12). In addition, the naphthalene diimide polymers cover the ITO substrate conformally (Figure 2.12). We further measured the work function of NDI-1 and crosslinked NDI-CL modified ITO using scanning Kevin probe microscopy (SKPM) with highly oriented pyrolytic graphite (HOPG) as the reference. We obtain uniform and homogeneous surface potential distributions with both NDI-1 and NDI-CL layers, which is beneficial for the charge collection at the interface (Figure 2.12).⁴⁷ We measured the work function of NDI-CL/ITO to be ~ 4.36 eV, which is lower than that of NDI-1/ITO (~ 4.55 eV), and in agreement with a previous report.⁴⁸ We performed drift-diffusion simulations with Solar Cell Capacitance Simulator (SCAPS)^{49,50} to understand the impact of the reduced work function of the electron-collecting electrode and found that the reduced work function will in theory, increase the device V_{OC} (Figure 2.13).



Figure 2.13: Drift-diffusion simulation results performed by SCAPS. (a) Schematics of energy diagram used for simulations. The influence of the work function of cathode on the device performance: (b) V_{OC} , (c) PCE, (d) FF and (e) J_{SC} . The simulation parameters for the perovskite were adopted from previous work³, and parameters of Spiro-OMeTAD are adopted from the literature.⁴ The blue and red dashed lines in (a) represent the measured work functions of NDI-1/ITO and NDI-CL/ITO. The blue and red diamonds in (b) and (c) stand for average data points of solar cell devices made using the NDI-1 and NDI-CL.

2.3.4 Solar Cell Device Architecture and Performance



Figure 2.14: (a) Device structure used in this study (n-i-p). (b) Statistical distribution of stabilized maximum power point (MPP). (c) Characteristic *J*-*V* curves (solid dots indicate reverse scan and hollow dots indicate forward scan) of perovskite solar cells based on NDI-1 and NDI-CL ETLs. (d) Statistical distribution of V_{OC} values obtained from reverse scans.

To compare device performance, we focused our analysis on the mixed-cation mixedhalide perovskite $FA_{0.83}Cs_{0.17}Pb(I_{0.83}Br_{0.15})_3$ (we denote as Cs17Br15, FA^+ = formamidinium), which has a bandgap of 1.63 eV.¹⁹ Figure 2.14a shows the n-i-p device architecture used in this study. As in the previous study of NDI-1, we utilized a sparse dispersion of Al₂O₃ nanoparticles on top of the naphthalene diimide polymers to improve wettability and obtain continuous perovskite films as the neat films of both polymers were hydrophobic (Figure 2.15).⁵¹ The Al₂O₃ nanoparticles should only cover partial of the surface area of the polymers and help improve wetting.⁵²



Figure 2.15: Water contact angles of NDI polymers on O₃ cleaned ITO. Harmonic meandetermined surface energies (γ_s) broken into their polar (γ_s^p) and dispersion (γ_s^d) components after O₃ cleaning of ITO and deposition of NDI polymers.

Sample	PCE (%)	$V_{\rm OC}$ (V)	FF (%)	$J_{\rm SC}~({ m mA/cm^2})$	MPP(%)
NDI-1	13.31 +/- 0.45	1.051 +/- 0.005	58.77 +/- 1.66	21.55 +/- 0.19	10.33 +/- 1.08
NDI-CL	15.10 +/- 0.62	1.077 +/- 0.003	64.43 +/- 2.38	21.76 +/- 0.28	12.28 +/- 0.73

Table 2.1: Photovoltaic figures of merit.



Figure 2.16: Additional photovoltaic parameters. (a) Comparison of (a) FF, (b) J_{SC} , (c) PCE, and (d) hysteresis of NDI-1 and NDI-CL devices based on reverse scan.

We used Spiro-OMeTAD as the hole transport layer (HTL) and gold as the top electrode. Figure 2.14c shows the characteristic *J-V* curves for NDI-1 and NDI-CL devices under 1 Sun illumination and clearly indicates that device using NDI-CL gives a higher V_{OC} than the device using NDI-1, as expected based on the work-function measurement. In addition, NDI-CL also reduces device hysteresis. We measure a maximum V_{OC} of ~1.08 V for NDI-CL solar cell. Figure 3b and 3d show the statistical distribution of maximum power point (MPP) and V_{OC} with all other photovoltaics parameters summarized in Table 2.1 and Figure 2.16. Overall, when using the crosslinked polymer, we see a consistent increase of V_{OC} (~ 30 mV on average) and FF, and thus PCE based on the reverse scan. The enhanced V_{OC} in NDI-CL-based solar cell devices is qualitatively consistent with the predictions from our SCAPS drift-diffusion simulations. We speculate that the enhanced FF might also be due to crosslinked NDI-CL blocking the shunting path between the perovskite and the ITO electrode or reduced non-radiative recombination at the polymer/perovskite interface (see below). Based on the lumped equivalent circuit model,⁵³ we estimate the shunt resistance of NDI-CL based perovskite solar cell to be $5270 \pm 350 \,\Omega \cdot \text{cm}^2$, which is double that of NDI-1 based device (2210 ± 210 $\Omega \cdot \text{cm}^2$, Figure 2.17). In addition, we obtain stabilized power outputs (SPO) efficiencies of ~ 12.28% and ~ 10.33% for solar cells using NDI-CL and NDI-1, respectively (Figure 2.14b and Table 2.1).



Figure 2.17: The shunt resistance of perovskite solar cell devices with NDI-1 and NDI-CL (based on reverse scan).

2.3.5 Perovskite Morphology and Photoluminescence (PL) Lifetime and Emission

To understand the differences in performance between NDI-1 and NDI-CL devices, we examined the influence of NDI-1 and NDI-CL on the quality of perovskite film formation. Figure 2.18a shows the X-ray diffraction (XRD) patterns of perovskite Cs17Br15 on top of NDI-1 and NDI-CL modified ITO substrates. The peak positions, full width at half maximum (FWHM), and peak intensities are indistinguishable, and we conclude therefore that the crystallinity of perovskite Cs17Br15 remains the same. In addition, the UV-vis absorption spectra show nearly identical absorption for Cs17Br15 films deposited on the two different substrates (Figure 2.18b). Figure 2.18c and 2.18d show the photoluminescence (PL) lifetime and PL emission of Cs17Br15 on NDI-1 and NDI-CL modified ITO substrates. We measure a longer lifetime (~74 ns) with stretched exponential fitting for perovskite on NDI-CL-modified ITO in comparison to that on NDI-1 (~25

ns) when excited from the ITO side with 640 nm wavelength. Accordingly, the PL emission of Cs17Br15 on NDI-CL is ~6.5 times higher than that of Cs17Br15 on NDI-1, which is consistent with enhanced PL lifetime, suggesting a potential reduction of defect density at the bottom interface. The suppressed non-radiative recombination may be due to a chemical passivation effect of NDI-CL, or simply reduced coupling between the NDI and perovskite due to the cinnamate, which may be partially responsible for the improved device performance observed with NDI-CL, especially improvements in the V_{OC} .



Figure 2.18: (a) XRD patterns, (b) UV-vis absorption spectra, (c) time-resolved PL (excited from ITO side with 640 nm laser) and (d) steady-state PL emission (excited from ITO side with 640 nm wavelength) of Cs17Br15 films coated on NDI-1 and NDI-CL.

The morphology and grain structure of perovskite films also play an important role in device performance.^{54,55} We use scanning electron microscopy (SEM) imaging to investigate the morphology of Cs17Br15 perovskite films deposited on NDI-1- and NDI-CL-modified ITO substrates. Figures 2.19a and 2.19b show top view SEM images of Cs17Br15 perovskite films on NDI-1 and NDI-CL. The perovskite films are dense and pin-hole free on both NDI-1- and NDI-

CL-modified ITO substrates with smooth and clean surfaces, indicating good film quality. Figures 2.19c and 2.19d show the corresponding grain size distributions for the two cases (approximating that SEM morphology corresponds to grain structure, while acknowledging that this approximation can be inaccurate⁵⁵). The average grain sizes we obtained from the SEM images (\sim 324 ± 99 nm *vs.* \sim 289 ± 108 nm) are similar for Cs17Br15 perovskite on NDI-1- and NDI-CL-modified ITO substrates. The surface roughness of the perovskite film on NDI-CL-modified ITO is ~13.6 nm, slightly lower than that of perovskite on NDI-1, which is ~18.5 nm (Figure 2.20). A slightly smoother perovskite film on NDI-CL should also be beneficial for device performance.



Figure 2.19: Top view SEM images of perovskite Cs17Br15 on (a) NDI-1 and (b) NDI-CL modified ITO substrates. Corresponding grain size distributions of perovskite Cs17Br15 on (c) NDI-1 and (d) NDI-CL modified ITO substrates.



Figure 2.20: AFM images of perovskite films on (a) NDI-1 and (b) NDI-CL.

2.4 Conclusions

In summary, we report a photo-crosslinkable naphthalene diimide copolymer as ETL for solution processed perovskite solar cells. The crosslinked ETL, NDI-CL, exhibits both high transparency of over 90% in the visible region, and high thermal stability (~ 300 °C). NDI-CL modified ITO shows a slightly lower work function than ITO modified with the non-crosslinked NDI-1. Our solar cell device results show that the crosslinked NDI-CL polymer leads to slightly higher V_{OC} , FF, PCE, and less hysteresis than its non-crosslinkable NDI-1 counterpart. The average V_{OC} is enhanced to ~1.08 V from ~ 1.05 V with stabilized PCE increasing to 12.28% from 10.33% on average. We ascribe the improved performance to the decreased work function of the NDI-CL modified ITO, and higher shunt resistance with crosslinked naphthalene diimide polymer-based perovskite solar cells. This work demonstrates that crosslinked polymer ETL works for perovskite solar cells.

2.5 References

- (1) National Renewable Energy Laboratory. Best Research-Cell Efficiencies , 2023. https://www.nrel.gov/pv/cell-efficiency.html (accessed 2023-07-28).
- (2) Lian, J.; Lu, B.; Niu, F.; Zeng, P.; Zhan, X. Electron-Transport Materials in Perovskite Solar Cells. *Small Methods* **2018**, *2* (10), 1–27.
- (3) Lin, L.; Jones, T. W.; Yang, T. C. J.; Duffy, N. W.; Li, J.; Zhao, L.; Chi, B.; Wang, X.; Wilson, G. J. Inorganic Electron Transport Materials in Perovskite Solar Cells. *Adv. Funct. Mater.* 2021, *31* (5), 2008300.
- (4) Leijtens, T.; Eperon, G. E.; Pathak, S.; Abate, A.; Lee, M. M.; Snaith, H. J. Overcoming Ultraviolet Light Instability of Sensitized TiO₂ with Meso-Superstructured Organometal Tri-Halide Perovskite Solar Cells. *Nat. Commun.* **2013**, *4*, 1–8.
- (5) Ranjan, S.; Ranjan, R.; Tyagi, A.; Rana, K. S.; Soni, A.; Kodali, H. K.; Dalal, V.; Singh, A.; Garg, A.; Nalwa, K. S.; Gupta, R. K. Low-Temperature Microwave Processed TiO₂ as an Electron Transport Layer for Enhanced Performance and Atmospheric Stability in Planar Perovskite Solar Cells. ACS Appl. Energy Mater. 2022, 5 (3), 2679–2696.
- (6) Zhou, H.; Chen, Q.; Li, G.; Luo, S.; Song, T. B.; Duan, H. S.; Hong, Z. R.; You, J. B.; Liu, Y.S.; Yang, Y. Interface Engineering of Highly Efficient Perovskite Solar Cells. *Science*. 2014, *345* (6196), 542–546.
- (7) Hu, W.; Yang, S.; Yang, S. Surface Modification of TiO₂ for Perovskite Solar Cells. *Trends Chem.* **2020**, *2* (2), 148–162.
- (8) Smith, J. A.; Game, O. S.; Bishop, J. E.; Spooner, E. L. K.; Kilbride, R. C.; Greenland, C.; Jayaprakash, R.; Alanazi, T. I.; Alanazi, T. I.; Cassella, E. J.; Tejada, A.; Tejada, A.; Chistiakova, G.; Wong-Stringer, M.; Routledge, T. J.; Parnell, A. J.; Hammond, D. B.; Lidzey, D. G. Rapid Scalable Processing of Tin Oxide Transport Layers for Perovskite Solar Cells. ACS Appl. Energy Mater. 2020, 3 (6), 5552–5562.
- (9) Anaraki, E. H.; Kermanpur, A.; Steier, L.; Domanski, K.; Matsui, T.; Tress, W.; Saliba, M.; Abate, A.; Grätzel, M.; Hagfeldt, A.; Correa-Baena, J. P. Highly Efficient and Stable Planar Perovskite Solar Cells by Solution-Processed Tin Oxide. *Energy Environ. Sci.* 2016, 9 (10), 3128–3134.
- (10) Luo, J.; Wang, Y.; Zhang, Q. Progress in Perovskite Solar Cells Based on ZnO Nanostructures. *Sol. Energy* **2018**, *163*, 289–306.
- (11) Liu, J.; Gao, C.; Luo, L.; Ye, Q.; He, X.; Ouyang, L.; Guo, X.; Zhuang, D.; Liao, C.; Mei, J.; Lau, W. Low-Temperature, Solution Processed Metal Sulfide as an Electron Transport Layer for Efficient Planar Perovskite Solar Cells. *J. Mater. Chem. A* 2015, *3* (22), 11750–11755.
- (12) Zhu, L.; Shao, Z.; Ye, J.; Zhang, X.; Pan, X.; Dai, S. Mesoporous BaSnO₃ Layer Based Perovskite Solar Cells. *Chem. Commun.* **2016**, *52* (5), 970–973.
- (13) Ling, X.; Yuan, J.; Liu, D.; Wang, Y.; Zhang, Y.; Chen, S.; Wu, H.; Jin, F.; Wu, F.; Shi, G.; Tang, X.; Zheng, J.; Liu, S.; Liu, Z.; Ma, W. Room-Temperature Processed Nb₂O₅ as the Electron-Transporting Layer for Efficient Planar Perovskite Solar Cells. ACS Appl. Mater. Interfaces 2017, 9 (27), 23181–23188.
- (14) Neophytou, M.; De Bastiani, M.; Gasparini, N.; Aydin, E.; Ugur, E.; Seitkhan, A.; Moruzzi, F.; Choaie, Y.; Ramadan, A. J.; Troughton, J. R.; Hallani, R.; Savva, A.; Tsetseris, L.; Inal, S.; Baran, D.; Laquai, F.; Anthopoulos, T. D.; Snaith, H. J.; De Wolf, S.; McCulloch, I. Enhancing the Charge Extraction and Stability of Perovskite Solar Cells Using Strontium

Titanate (SrTiO₃) Electron Transport Layer. *ACS Appl. Energy Mater.* **2019**, 2(11), 8090-8097.

- (15) Jameel, M. A.; Yang, T. C. J.; Wilson, G. J.; Evans, R. A.; Gupta, A.; Langford, S. J. Naphthalene Diimide-Based Electron Transport Materials for Perovskite Solar Cells. J. *Mater. Chem. A* 2021, 9 (48), 27170–27192.
- (16) Wang, J.; Fu, W.; Jariwala, S.; Sinha, I.; Jen, A. K. Y.; Ginger, D. S. Reducing Surface Recombination Velocities at the Electrical Contacts Will Improve Perovskite Photovoltaics. *ACS Energy Lett.* **2019**, *4* (1), 222–227.
- (17) Yoon, H.; Kang, S. M.; Lee, J. K.; Choi, M. Hysteresis-Free Low-Temperature-Processed Planar Perovskite Solar Cells with 19.1% Efficiency. *Energy Environ. Sci.* 2016, 9 (7), 2262–2266.
- (18) Heo, J. H.; Han, H. J.; Kim, D.; Ahn, T. K.; Im, S. H. Hysteresis-Less Inverted CH₃NH₃PbI₃ Planar Perovskite Hybrid Solar Cells with 18.1% Power Conversion Efficiency. *Energy Environ. Sci.* **2015**, *8* (5), 1602–1608.
- (19) Shi, Y.; Rojas-Gatjens, E.; Wang, J.; Pothoof, J.; Giridharagopal, R.; Ho, K.; Jiang, F.; Taddei, M.; Yang, Z.; Sanehira, E. M.; Irwin, M. D.; Silva-Acuña, C.; Ginger, D. S. (3-Aminopropyl)Trimethoxysilane Surface Passivation Improves Perovskite Solar Cell Performance by Reducing Surface Recombination Velocity. ACS Energy Lett. 2022, 4081– 4088.
- (20) Jung, S. K.; Lee, D. S.; Ann, M. H.; Im, S. H.; Kim, J. H.; Kwon, O. P. Non-Fullerene Organic Electron-Transporting Materials for Perovskite Solar Cells. *ChemSusChem* 2018, *11* (22), 3882–3892.
- (21) Warby, J.; Zu, F.; Zeiske, S.; Gutierrez-partida, E.; Frohloff, L.; Frohna, K.; Mosconi, E.; Radicchi, E.; Lang, F.; Shah, S.; Peña-, F.; Hempel, H.; Unold, T.; Koch, N.; Armin, A.; Angelis, F. De; Stranks, S.; Neher, D.; Stolterfoht, M. Understanding Performance Limiting Interfacial Recombination in Pin Perovskite Solar Cells. *Accept. Adv. Energy Mater.* 2022, 2103567, 1–10.
- Wojciechowski, K.; Ramirez, I.; Gorisse, T.; Dautel, O.; Dasari, R.; Sakai, N.; Hardigree, J. M.; Song, S.; Marder, S.; Riede, M.; Wantz, G.; Snaith, H. J. Cross-Linkable Fullerene Derivatives for Solution-Processed n-i-p Perovskite Solar Cells. ACS Energy Lett. 2016, 1 (4), 648–653.
- (23) Bai, Y.; Dong, Q.; Shao, Y.; Deng, Y.; Wang, Q.; Shen, L.; Wang, D.; Wei, W.; Huang, J. Enhancing Stability and Efficiency of Perovskite Solar Cells with Crosslinkable Silane-Functionalized and Doped Fullerene. *Nat. Commun.* **2016**, *7*, 1–9.
- (24) Jiang, K.; Wu, F.; Zhu, L.; Yan, H. Naphthodiperylenetetraimide-Based Polymer as Electron-Transporting Material for Efficient Inverted Perovskite Solar Cells. ACS Appl. Mater. Interfaces 2018, 10 (42), 36549–36555.
- (25) Chen, C.; Cheng, M.; Li, H.; Qiao, F.; Liu, P.; Li, H.; Kloo, L.; Sun, L. Molecular Engineering of Ionic Type Perylenediimide Dimer-Based Electron Transport Materials for Efficient Planar Perovskite Solar Cells. *Mater. Today Energy* 2018, 9, 264–270.
- (26) Jung, S. K.; Heo, J. H.; Lee, D. W.; Lee, S. H.; Lee, S. C.; Yoon, W.; Yun, H.; Kim, D.; Kim, J. H.; Im, S. H.; Kwon, O. P. Homochiral Asymmetric-Shaped Electron-Transporting Materials for Efficient Non-Fullerene Perovskite Solar Cells. *ChemSusChem* **2019**, *12* (1), 224–230.
- (27) Jung, S. K.; Heo, J. H.; Lee, D. W.; Lee, S. C.; Lee, S. H.; Yoon, W.; Yun, H.; Im, S. H.; Kim, J. H.; Kwon, O. P. Nonfullerene Electron Transporting Material Based on

Naphthalene Diimide Small Molecule for Highly Stable Perovskite Solar Cells with Efficiency Exceeding 20%. *Adv. Funct. Mater.* **2018**, *28* (20).

- (28) Kim, H. II; Kim, M. J.; Choi, K.; Lim, C.; Kim, Y. H.; Kwon, S. K.; Park, T. Improving the Performance and Stability of Inverted Planar Flexible Perovskite Solar Cells Employing a Novel NDI-Based Polymer as the Electron Transport Layer. *Adv. Energy Mater.* 2018, 8 (16), 1–7.
- (29) Zhu, Z.; Zhao, D.; Chueh, C. C.; Shi, X.; Li, Z.; Jen, A. K. Y. Highly Efficient and Stable Perovskite Solar Cells Enabled by All-Crosslinked Charge-Transporting Layers. *Joule* 2018, 2 (1), 168–183.
- (30) Zhao, D.; Zhu, Z.; Kuo, M. Y.; Chueh, C. C.; Jen, A. K. Y. Hexaazatrinaphthylene Derivatives: Efficient Electron-Transporting Materials with Tunable Energy Levels for Inverted Perovskite Solar Cells. *Angew. Chemie Int. Ed.* **2016**, *55* (31), 8999–9003.
- (31) Quinn, J. T. E.; Zhu, J.; Li, X.; Wang, J.; Li, Y. Recent Progress in the Development of N-Type Organic Semiconductors for Organic Field Effect Transistors. J. Mater. Chem. C 2017, 5 (34), 8654–8681.
- (32) Bhosale, S. V.; Jani, C. H.; Langford, S. J. Chemistry of Naphthalene Diimides. *Chem. Soc. Rev.* **2008**, *37* (2), 331–342.
- (33) Nowak-Król, A.; Shoyama, K.; Stolte, M.; Würthner, F. Naphthalene and Perylene Diimides-Better Alternatives to Fullerenes for Organic Electronics? *Chem. Commun.* 2018, 54 (98), 13763–13772.
- (34) Li, F.; Deng, X.; Qi, F.; Li, Z.; Liu, D.; Shen, D.; Qin, M.; Wu, S.; Lin, F.; Jang, S. H.; Zhang, J.; Lu, X.; Lei, D.; Lee, C. S.; Zhu, Z.; Jen, A. K. Y. Regulating Surface Termination for Efficient Inverted Perovskite Solar Cells with Greater Than 23% Efficiency. J. Am. Chem. Soc. 2020, 142 (47), 20134–20142.
- (35) Heo, J. H.; Im, S. H.; Noh, J. H.; Mandal, T. N.; Lim, C. S.; Chang, J. A.; Lee, Y. H.; Kim, H. J.; Sarkar, A.; Nazeeruddin, M. K.; Grätzel, M.; Seok, S. II. Efficient Inorganic-Organic Hybrid Heterojunction Solar Cells Containing Perovskite Compound and Polymeric Hole Conductors. *Nat. Photonics* 2013, 7 (6), 486–491.
- (36) Zhao, D.; Sexton, M.; Park, H. Y.; Baure, G.; Nino, J. C.; So, F. High-Efficiency Solution-Processed Planar Perovskite Solar Cells with a Polymer Hole Transport Layer. *Adv. Energy Mater.* 2015, 5 (6), 1–5.
- Liu, D.; Li, Y.; Yuan, J.; Hong, Q.; Shi, G.; Yuan, D.; Wei, J.; Huang, C.; Tang, J.; Fung, M. K. Improved Performance of Inverted Planar Perovskite Solar Cells with F4-TCNQ Doped PEDOT:PSS Hole Transport Layers. J. Mater. Chem. A 2017, 5 (12), 5701–5708.
- Jung, E. H.; Jeon, N. J.; Park, E. Y.; Moon, C. S.; Shin, T. J.; Yang, T. Y.; Noh, J. H.; Seo, J. Efficient, Stable and Scalable Perovskite Solar Cells Using Poly(3-Hexylthiophene). *Nature* 2019, 567 (7749), 511–515.
- (39) Tremblay, M. H.; Schutt, K.; Zhang, Y.; Lim, J.; Lin, Y. H.; Warby, J. H.; Barlow, S.; Snaith, H. J.; Marder, S. R. A Photo-Crosslinkable Bis-Triarylamine Side-Chain Polymer as a Hole-Transport Material for Stable Perovskite Solar Cells. *Sustain. Energy Fuels* 2019, 4 (1), 190–198.
- (40) Zuniga, C. A.; Barlow, S.; Marder, S. R. Approaches to Solution-Processed Multilayer Organic Light-Emitting Diodes Based on Cross-Linking. *Chem. Mater.* 2011, 23 (3), 658– 681.
- (41) Zhang, Y. D.; Hreha, R. D.; Jabbour, G. E.; Kippelen, B.; Peyghambarian, N.; Marder, S. R. Photo-Crosslinkable Polymers as Hole-Transport Materials for Organic Light-Emitting

Diodes. J. Mater. Chem. 2002, 12 (6), 1703–1708.

- (42) Sung, S. J.; Cho, K. Y.; Hah, H.; Lee, J.; Shim, H. K.; Park, J. K. Two Different Reaction Mechanisms of Cinnamate Side Groups Attached to the Various Polymer Backbones. *Polymer (Guildf)*. **2006**, *47* (7), 2314–2321.
- (43) Al Kurdi, K.; McCarthy, D. P.; McMeekin, D. P.; Furer, S. O.; Tremblay, M. H.; Barlow, S.; Bach, U.; Marder, S. R. A Naphthalene Diimide Side-Chain Polymer as an Electron-Extraction Layer for Stable Perovskite Solar Cells. *Mater. Chem. Front.* 2021, 5 (1), 450–457.
- (44) Un, H. I.; Gregory, S. A.; Mohapatra, S. K.; Xiong, M.; Longhi, E.; Lu, Y.; Rigin, S.; Jhulki, S.; Yang, C. Y.; Timofeeva, T. V.; Wang, J. Y.; Yee, S. K.; Barlow, S.; Marder, S. R.; Pei, J. Understanding the Effects of Molecular Dopant on N-Type Organic Thermoelectric Properties. *Adv. Energy Mater.* 2019, 9 (24), 1–10.
- (45) Kim, M. J.; Lee, M.; Min, H.; Kim, S.; Yang, J.; Kweon, H.; Lee, W.; Kim, D. H.; Choi, J. H.; Ryu, D. Y.; Kang, M. S.; Kim, B. S.; Cho, J. H. Universal Three-Dimensional Crosslinker for All-Photopatterned Electronics. *Nat. Commun.* 2020, *11* (1), 1–11.
- (46) Guo, Y.; Sato, W.; Inoue, K.; Zhang, W.; Yu, G.; Nakamura, E. N-Type Doping for Efficient Polymeric Electron-Transporting Layers in Perovskite Solar Cells. J. Mater. Chem. A 2016, 4 (48), 18852–18856.
- (47) Chen, H.; Maxwell, A.; Li, C.; Teale, S.; Chen, B.; Zhu, T.; Ugur, E.; Harrison, G.; Grater, L.; Wang, J.; Wang, Z.; Zeng, L.; Park, S. M.; Chen, L.; Serles, P.; Awni, R. A.; Subedi, B.; Zheng, X.; Xiao, C.; Podraza, N. J.; Filleter, T.; Liu, C.; Yang, Y.; Luther, J. M.; De Wolf, S.; Kanatzidis, M. G.; Yan, Y.; Sargent, E. H. Regulating Surface Potential Maximizes Voltage in All-Perovskite Tandems. *Nature* 2023, *613* (7945), 676–681.
- (48) Fürer, S. O.; Rietwyk, K. J.; Pulvirenti, F.; McMeekin, D. P.; Surmiak, M. A.; Raga, S. R.; Mao, W.; Lin, X.; Hora, Y.; Wang, J.; Shi, Y.; Barlow, S.; Ginger, D. S.; Marder, S. R.; Bach, U. Naphthalene-Imide Self-Assembled Monolayers as a Surface Modification of ITO for Improved Thermal Stability of Perovskite Solar Cells. *ACS Appl. Energy Mater.* 2023, 6 (2), 667–677.
- (49) Burgelman, M.; Decock, K.; Khelifi, S.; Abass, A. Advanced Electrical Simulation of Thin Film Solar Cells. *Thin Solid Films* **2013**, *535* (1), 296–301.
- (50) Burgelman, M.; Nollet, P.; Degrave, S. Modelling Polycrystalline Semiconductor Solar Cells. *Thin Solid Films* **2000**, *361*, 527–532.
- (51) Taddei, M.; Smith, J. A.; Gallant, B. M.; Zhou, S.; Westbrook, R. J. E.; Shi, Y.; Wang, J.; Drysdale, J. N.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Snaith, H. J.; Ginger, D. S. Ethylenediamine Addition Improves Performance and Suppresses Phase Instabilities in Mixed-Halide Perovskites. 2022, 7(12), 4265-4273.
- (52) Jin, H.; Farrar, M. D.; Ball, J. M.; Dasgupta, A.; Caprioglio, P.; Narayanan, S.; Oliver, R. D. J.; Rombach, F. M.; Putland, B. W. J.; Johnston, M. B.; Snaith, H. J. Alumina Nanoparticle Interfacial Buffer Layer for Low-Bandgap Lead-in Perovskite Solar Cells. *Adv. Funct. Mater.* 2023.
- (53) Lee, J.; Baik, S. Enhanced Crystallinity of CH₃NH₃PbI₃ by the Pre-Coordination of PbI₂-DMSO Powders for Highly Reproducible and Efficient Planar Heterojunction Perovskite Solar Cells. *RSC Adv.* **2018**, *8* (2), 1005–1013.
- (54) Saliba, M.; Correa-Baena, J. P.; Grätzel, M.; Hagfeldt, A.; Abate, A. Perovskite Solar Cells: From the Atomic Level to Film Quality and Device Performance. *Angew. Chemie - Int. Ed.* 2018, *57* (10), 2554–2569.

- (55) Jariwala, S.; Sun, H.; Adhyaksa, G. W. P.; Lof, A.; Muscarella, L. A.; Ehrler, B.; Garnett, E. C.; Ginger, D. S. Local Crystal Misorientation Influences Non-Radiative Recombination in Halide Perovskites. *Joule* 2019, *3* (12), 3048–3060.
- (56) Valverde-Chávez, D. A.; Rojas-Gatjens, E.; Williamson, J.; Jariwala, S.; Shi, Y.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Ginger, D. S.; Silva-Acuña, C. Nonlinear Photocarrier Dynamics and the Role of Shallow Traps in Mixed-Halide Mixed-Cation Hybrid Perovskites. *J. Mater. Chem. C* 2021, *9* (26), 8204–8212.
- (57) Pothoof, J.; Westbrook, R. J. E.; Giridharagopal, R.; Breshears, M. D.; Ginger, D. S. Surface Passivation Suppresses Local Ion Motion in Halide Perovskites. *J. Phys. Chem. Lett.* **2023**, 6092–6098.
- (58) Jena, A. K.; Numata, Y.; Ikegami, M.; Miyasaka, T. Role of Spiro-OMeTAD in Performance Deterioration of Perovskite Solar Cells at High Temperature and Reuse of the Perovskite Films to Avoid Pb-Waste. *J. Mater. Chem. A* **2018**, *6* (5), 2219–2230.

3 Highly Emissive and Defect-Free Perovskite Films: Design Rules Towards New Passivation Molecules



Figure 3.1: Graphical abstract depicting selected molecules or groups of molecules examined to understand design rules of passivation molecules.

This project was a collaboration with Brieuc Le Dé, Esteban Rojas-Gatjens, Sarthak Jariwala, Yangwei Shi, Ashley Marshall, Jian Wang, James Drysdale, and Joel Smith. Brieuc Le Dé and Esteban Rojas-Gatjens helped with FA_{0.83}Cs_{0.17}Pb(I_{0.85}Br_{0.15}) (Cs17Br15) film preparation and passivator screening. James Drysdale, Ashley Marshall, and Joel Smith helped with screening passivators on FA_{0.7}Cs_{0.3}PbI₃, FA_{0.83}Cs_{0.17}Pb(I_{0.75}Br_{0.25})₃ (Cs17Br25), and CsPbI₂Br films. Sarthak Jariwala, Jian Wang, and Yangwei Shi helped to screen passivators on MAPbI₃, Cs17Br15 and Cs17Br25 films. Yangwei Shi also prepared and optimized photovoltaic devices.

This work was supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technology Office (SETO), Award Number DE-EE0008747, and the Office of Naval Research (ONR), Award Number N00014-20-1-2587. I also wish to acknowledge support of this project by the Department of Education Graduate Assistance in Areas of National Need (GAANN) program at Georgia Institute of Technology (Award #P200A180075).

3.1 Introduction

As discussed in chapter 1, lead halide perovskites (LHPs) have rapidly emerged as materials of significant interest for a variety of optoelectronic applications, especially solar cells.¹⁻⁵ LHPs can be processed into thin films via relatively simple solution processing techniques such as spin-coating, yet possess numerous favorable optoelectronic properties such as tunable bandgaps, low exciton binding energies, large absorption coefficients, high ambipolar charge mobilities, and long charge diffusion lengths.⁶⁻⁹ Improvements to device performance and stability have been achieved through various material and device engineering approaches such as absorber layer compositional engineering, design of new of charge selective layers, and surface passivation. Despite considerable research, it remains an outstanding challenge to further decrease non-radiative losses to approach the theoretical performance limits and achieve maximum $V_{\rm OC}$ —especially at the top interface with C₆₀ within inverted (p-i-n) perovskite solar cells.¹⁰

While most semiconductors are highly sensitive to defects,¹¹ LHPs have widely been described as "defect-tolerant" materials.¹² Nevertheless, defects in the bulk and at the surfaces of films can be detrimental to device performance. Defects can occur as a result of imperfections in the lattice consisting of vacancies (vacant lattice sites that are missing atoms/molecules), interstitials (extra atoms/molecules at a site in the lattice where there is not usually an atom), and antisite substitutions (incorrect atoms/molecules occupying lattice sites).¹³ The presence of these defects produces traps or energetic states within the bandgap of the perovskite that enhance the rate of non-radiative recombination. Additionally, non-radiative recombination can be induced from interfaces by contact with transport layers¹⁴— the perovskite/C₆₀ interface-induced traps of p-i-n cells account for the greatest loss within state-of-the-art cells.¹⁵ To achieve the maximum

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open circuit voltage (V_{OC}) for a semiconductor material in a solar cell, non-radiative recombination pathways must be minimized.¹⁶

A range of passivation approaches have been explored towards optimizing the efficiency and stability of PSCs. The predominant approach in the literature involves the use of various substituted ammonium cations, which are thought to fill A-site vacancies,¹⁷ but can in some cases induce the formation of 2D perovskites at the interface.¹⁸⁻¹⁹ A similar, but distinct approach involves the use of neutral amine additives,²⁰⁻²¹ where any amine can take part in proton exchange with MA⁺ and FA⁺, but it has recently been reported that primary and secondary amines are capable of reacting with formamidinium precursors in solution and on the surface.²²⁻²³ Other Lewis bases have been employed with the aim of coordinating otherwise undercoordinated Pb ions.²⁴ Various other approaches include the use of halogen bonding derivatives,²⁵ molecules with acidic functional groups,²⁶ and zwitterions.²⁷

Clearly, extensive empirical observations on the passivation of perovskites have been reported with marked increases in efficiency and stability; however, systematic studies examining a variety of functional groups or isolating a single variable are less common.²⁸⁻³⁰ Furthermore, efficient passivation approaches for MA-free perovskites, which offer superior stability to their MA-containing counterparts, are relatively underexplored to date.³¹ This work examines passivation effects across a series of molecules and across a series of varying perovskite compositions, including MA-free wide-bandgap perovskites, in order to attempt to identify further variables specific to the defects that can be present in a given composition. We examine a "core" series of benzylamines and benzylammonium salts, while controlling for several variables: degree of methylation of amine, degree of methylation of ammonium, and the counterion of the ammonium salts. Additionally, we survey several other "families" of

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compounds consisting of various Lewis bases, as well as amines and ammoniums with redoxactive moieties to facilitate charge extraction.

3.2 Experimental

Materials and methods:

All precursors were used without further purification and were stored and prepared in a nitrogen-filled glovebox. Formamidinium iodide (FAI, Greatcell), Cesium iodide (CsI, 99.999% metal basis, Alfa Aesar), lead iodide (PbI₂, perovskite grade, Tokyo Chemical Industries ltd (TCI)) and lead bromide (PbBr₂, 99.998% metals basis, Alfa Aesar) were dissolved in a mixture of anhydrous N,N-Dimethylformamide (DMF, Sigma) and anhydrous dimethyl sulfoxide (DMSO, Sigma) with a volume ratio of 4:1 to prepare a 1.2 M solution of FA_{0.83}Cs_{0.17}Pb(I_{0.75}Br_{0.25})₃ or FA_{0.83}Cs_{0.17}Pb(I_{0.75}Br_{0.15})₃ according to stoichiometry.

MeO-2PACz and Me-4PACz were purchased from TCI. Patterned indium tin oxide (ITO, from Xin Yan Technology ltd) glass substrates and glass substrates (purchased from VWR) were cleaned by sequentially sonicating in water containing ~2% Micro-90 detergent, deionized water, acetone, and isopropanol (IPA) for 10 mins, respectively, followed by UV-Ozone cleaning for 23 minutes. The perovskite precursor solution was dissolved and stored in the glovebox before spincoating. The perovskite ink was filtered with a 0.2 μ m PTFE filter before use and 40 μ L of the solution was deposited on top of the substrate and spin-coated for 10 s at 1000 rpm (200 rpm/s) and 35 s at 5000 rpm (800rpm/s). 330 μ L anhydrous anisole (Sigma) antisolvent, filtered with 0.45 μ m PTFE filter, was dropped from above when 5s remained. The perovskite films were then annealed at 100 °C for 40 mins. The preparation of perovskite films was performed in a nitrogen-filled glovebox.

Solar cell fabrication (Cs17Br25):

For the device structure used in this study, Me-4PACz (TCI) was used as the hole transport layer and was prepared with a concentration of 0.5 mg/mL in anhydrous ethanol (Sigma). 100 µL of the HTL solution was deposited onto the ITO substate before spin-coating with 3000 rpm for 30 s, followed annealing at 100 °C for 10 mins inside of the glovebox. To obtain continuous perovskite films, Al₂O₃ (Sigma, diluted in IPA with 1:150 volume ratio) nanoparticle was dynamically spun onto the substrates and then annealed for ~ 2 mins. The perovskite films were deposited in the same as mentioned above. The BzAOTs and BzAOTf molecules were dissolved in anhydrous isopropanol with a concentration of 10 mM. The interlayer solutions were dynamically spin-coated onto the perovskite films at 3000 rpm for 30s without further annealing. The control devices were dynamically spin-coated with IPA solution to exclude the impact of IPA solvent. After that, 30 nm C_{60} and 5 nm Bathocuproine (BCP) were thermally evaporated onto the perovskite layer. For C_{60} , the deposition rate was from 0.2 Å/s for 5 nm to 0.5 Å/s for the rest of the total 25 nm. The deposition rate for BCP was 0.2 Å/s. 100 nm Ag was then thermally evaporated with an evaporation rate of 0.5 Å/s for the first 10 nm to 1 Å/s for the rest of the 90 nm.

Solar cell fabrication (Cs17Br15):

To fabricate the Cs17Br15 devices, an HTL solution (MeO-2PACz, TCI) was prepared with a concentration of 1 mmol/L in anhydrous ethanol.¹ 100 μ L of the solution was put onto the ITO substate before spin-coating with 3000 rpm for 30 s. The substrates were then annealed at 100 °C for 10 mins. The perovskite films were deposited in the same manner as described above.² BAI, NBAI, and NNBAI surface passivation solutions (10mM in IPA) were dynamically spincoated onto the perovskite films at 3000 rpm for 30s without further annealing. After perovskite deposition and surface passivation, 30 nm C_{60} and 5 nm Bathocuproine (BCP) were thermally evaporated onto the perovskite layer. For C_{60} , the deposition rate was from 0.2 Å/s for 5nm to 0.5 Å/s for the rest of the total 25 nm. The deposition rate for BCP was 0.2 Å/s. Finally, 100 nm Ag was thermally evaporated with an evaporation rate of 0.5 Å/s for the first 10 nm, and increased to 1 Å/s for the remaining 90 nm.

Solar Cell Performance Testing:

For solar cell performance measurement, current-voltage (*J-V*) scans under 1 Sun equivalent illumination were measured using an ORIEL LSH-7320 ABA LED solar simulator in a nitrogen-filled glovebox, which is calibrated with Silicon reference solar cell certified by NREL. The effective area of the solar cell is 0.0453 cm². *J-V* scans were performed with a Keithley 2400 controlled by a LabView program. The voltage values are scanned at a 0.02 V step in the range of -0.1 V to 1.24 V. The steady-state power output was carried out by measuring the solar cells under the bias of the maximum power point (MMP) and 1 Sun intensity.

Photoluminescence quantum efficiency (PLQE):

PLQE results are determined using a 532 nm continuous wave laser (CrystaLaser LC) as the excitation source to illuminate the samples in an integrating sphere (Hamamatsu photonics K.K). The beam intensity was fixed equal to 60 mW/cm². The power density was verified using an optical beam profiler. The PLQE is calculated using the following formula:

$$PLQ = \frac{I_{em,sample} - I_{em. \ blank}}{I_{exc,blank} - I_{exc,sample}} * 100$$
 Equation 3.1

Where $I_{em,sample}$ and $I_{em,blank}$ are the integrated area under the curve in the emission region (650-950 nm) of the sample and the bare glass blank, respectively. The $I_{exc,sample}$ and $I_{exc,blank}$ are the integrated area under the curve in the excitation region (450-630 nm) of the sample and the bare glass blank respectively.

Time Resolved Photoluminescence:

The TRPL spectra at 405 nm excitation were acquired using an Edinburgh FLS1000 spectrometer with EPL-405, a 405 nm picosecond pulsed diode laser. The repetition rate is controlled by an internal trigger input and was set to 1 MHz. The emission and excitation slits were controlled to have an emission signal frequency of 1 to 2% of the start rate. The slits were kept constant for all measurements and the film stage was moved in the x-direction to maximize the emission. A PMT-900 detector was used in TCSPC mode with an instrumental response width of approximately 600 ps.

Synthesis of Passivation Materials:

N-methylbenzylammonium iodide (NBAI)



Figure 3.2: Synthesis of *N*-methylbenzylammonium iodide (NBAI).

N-methylbenzylammonium iodide (NBAI): ¹H NMR (400 MHz, DMSO-d6) δ 8.66 (s, 2H), 7.51 – 7.39 (m, 5H), 4.13 (s, 2H), 2.58 (s, 3H). Anal. Calcd for C₈H₁₂NI: C, 38.57; H, 4.86; N, 5.62. Found: C, 38.67; H, 5.01; N, 5.60.



Figure 3.3: ¹H-NMR of *N*-methylbenzylammonium iodide (NBAI).

N,N-dimethylbenzylammonium iodide (NNBAI)



Figure 3.4: Synthesis of *N*,*N*-dimethylbenzylammonium iodide (NNBAI).

N,*N*-dimethylbenzylammonium iodide (NNBAI): ¹H NMR (500 MHz, CDCl₃) δ 7.67 – 7.59 (m, 2H), 7.53 – 7.44 (m, 3H), 4.20 (s, 2H), 2.74 (s, 7H). Anal. Calcd for C₉H₁₄NI: C, 41.08; H, 5.36; N, 5.32. Found: C, 41.27; H, 5.34; N, 5.32.



Figure 3.5: ¹H-NMR of *N*,*N*-dimethylbenzylammonium iodide (NNBAI).

N,*N*,*N*-trimethylbenzylammonium iodide (NNNBAI)



Figure 3.6: Synthesis of *N*,*N*,*N*-trimethylbenzylammonium iodide (NNNBAI).

N,*N*,*N*-trimethylbenzylammonium iodide (NNNBAI): ¹H NMR (400 MHz, D₂O) δ 7.63 – 7.48 (m, 5H), 4.48 (s, 2H), 3.08 (s, 9H). Anal. Calcd for C₁₀H₁₆NI: C, 43.34; H, 5.82; N, 5.05. Found: C, 43.38; H, 5.82; N, 5.04.



Figure 3.7: ¹H-NMR of *N*,*N*,*N*-trimethylbenzylammonium iodide (NNNBAI).

Benzylammonium triflate (BAOTf):



Figure 3.8: Synthesis of benzylammonium triflate (BAOTf).

Benzylammonium triflate (BAOTf): ¹H NMR (500 MHz, DMSO-d6) δ 8.06 (s, 3H), 7.48 – 7.35

(m, 5H), 4.04 (s, 2H). ^{19}F NMR (471 MHz, DMSO-d6) δ -77.75. Anal. Calcd for

C₈H₁₀F₃NO₃S: C, 37.36; H, 3.92; N, 5.45. Found: C, 37.46; H, 3.91; N, 5.34.



Figure 3.9: ¹H-NMR of benzylammonium triflate (BAOTf).



Figure 3.10: ¹⁹F-NMR of benzylammonium triflate (BAOTf).

Benzylammonium Tosylate (BAOTs)



Figure 3.11: Synthesis of benzylammonium tosylate (BAOTs).

Benzylammonium Tosylate (BAOTs):¹H NMR (500 MHz, DMSO-d6) δ 8.06 (s, 3H), 7.50 – 7.43 (m, 5H), 7.44 – 7.34 (m, 2H), 7.11 (dt, *J* = 7.7, 0.7 Hz, 2H), 4.03 (s, 2H), 2.29 (s, 3H). Anal. Calcd for C₁₄H₁₇NO₃S: C, 60.19; H, 6.13; N, 5.01. Found: C, 59.98; H, 6.18; N, 5.00.



Figure 3.12: ¹H-NMR of benzylammonium tosylate (BAOTs).

Benzylammonium Tetrafluoroborate (BABF4)



Figure 3.13: Synthesis of benzylammonium tetrafluoroborate (BABF₄).

Benzylammonium Tetrafluoroborate (BABF₄): ¹H NMR (500 MHz, CD₃CN) δ 7.50 – 7.40 (m, 5H), 6.43 (s, 3H), 4.15 (s, 2H). ¹⁹F NMR (471 MHz, CD₃CN) δ -151.43, -151.48. Anal. Calcd for C₇H₁₀BF₄N: C, 43.12; H, 5.17; N, 7.18. Found: C, 43.33; H, 5.26; N, 7.17.



Figure 3.14: ¹H-NMR of benzylammonium tetrafluoroborate (BABF₄).



Figure 3.15: ¹⁹F-NMR of benzylammonium tetrafluoroborate (BABF₄).

3.3 Results and Discussion

3.3.1 Scope of Passivation Molecules



Figure 3.16: Benzylamine-based passivation molecules (left) and other passivation molecules (right) selected and synthesized (where necessary) for study.

Our passivation studies largely centered around benzylamine derivatives and benzylammonium salts, which have been extensively reported in the literature to passivate and improve the stability of lead-halide perovskites.^{20, 32-33} We selected these molecules to systematically examine whether the previously reported passivation effects are imparted by the cation, the corresponding neutral amine, the (pseudo)halide counterion, or some combination or reaction product of these species. Examining neutral amines with otherwise identical extents of *N*-methylation allowed us to examine the importance of the protonation state of the amine. Several other salts and Lewis basic compounds were also screened for their efficacy.

Varying the counterion enables several new research possibilities. Notably most commercial alkylammonium and phenylalkylammonium halides are virtually insoluble in chloroform, making the study of the effect of deposition solvent with a single passivation salt near-impossible. Some counterions, such as tosylate, increase the lipophilicity of the salt and enable deposition from relatively more non-polar solvents such as chloroform. Indirectly this approach can allow one to examine the importance of the deposition solvent, where previous studies have emphasized the possible surface reconstruction when depositing passivators from isopropyl alcohol.³⁴ Other counterions may be able to induce a surface dipole, which could affect the workfunction of the perovskite. Finally, different counterions may enable different types of intermolecular interactions such as chelation or hydrogen bonding, or offer other properties such as non-coordination or intrinsic thermal stability.

A variety of potential imperfections can exist with the lattice and at surface terminations. Cationic species may interact with A-site vacancies, neutral amines may either become protonated and thus act like their cationic counterparts or fill halide vacancies by coordinating undercoordinated lead, and anionic species may also fill halide vacancies. Increasing the degree of methylation of the benzylammonium iodide salts will decrease the quantity of hydrogen bond donors within the cation. This could in turn impact the ability of the cationic species to form 2Dperovskite heterostructures at the surface. Quaternary ammonium salts exhibit improved solubility in lower polarity solvents such as chloroform, which may increase their processing window. Additionally, quaternary ammonium salts cannot be readily deprotonated, which may improve their stability and prevent equilibria involving formation of the neutral basic amines in solution.

3.3.2 Synthesis and Characterization of Passivation Molecules

Benzylamine, *N*-methyl-benzylamine, *N*,*N*-benzylamine, (3aminopropyl)trimethoxysilane, (N-methylaminopropyl)trimethoxysilane, (*N*,*N*dimethylaminopropyl)trimethoxysilane, triphenylmethanethiol, triphenylphosphine sulfide, and cetrimmonium bromide were purchased from commercial sources and their purities were verified by ¹H-NMR spectroscopy. Benzylammonium iodide (BAI), N-methylbenzylammonium (NBAI), N,N-

dimethylammonium iodide (NNBAI), benzylammonium bromide (BABr), and benzylammonium chloride (BACl) salts were synthesized by protonation of benzylamine with the appropriate acids according to a procedure from the literature.³⁵ *N*,*N*,*N*-trimethylbenzylammonium iodide (NNNBAI) was synthesized by quaternization of *N*,*N*-dimethylbenzylamine with methyl iodide according to a literature procedure.³⁶ Benzylammonium trifluoromethylsulfonate (BAOTf), benzylammonium *p*-toluenesulfonate (BAOTs), and benzylammonium tetrafluoroborate (BABF4) were synthesized by protonation of benzylamine with the appropriate acids via modified literature procedures.³⁷

3.3.3 Scope of Perovskite Compositions

In addition to systematically screening passivation agents, we also sought to examine the impact of the agents across a series of perovskite compositions. Prior passivation studies have largely focused on single perovskite compositions; however, the composition may influence the type or density of traps. We selected two wide-bandgap tandem-relevant MA-free mixed-halide perovskites as the core compositions—Cs17Br15 and Cs17Br25, shown in Table 3.1. MA-free compositions have been demonstrated to exhibit superior stability to their MA-containing counterparts, addressing a critical issue towards hybrid perovskite commercialization.³⁸ Historically, the V_{oC} of wide bandgap perovskites has been limited by their radiative efficiency and identifying efficient passivation approaches towards this compositional space has proven more elusive.^{31, 39-40} We also screened a formamidinium-cesium triiodide perovskite where halide vacancies can only take the form of iodide vacancies and halide migration is nonexistent. Finally, we screened an all-inorganic ultra-wide bandgap perovskite, CsPbI₂Br, where A-site

defects could only involve cesium. The archetypal MAPbI₃ (MAPI) perovskite is included for comparison.

Perovskite	Bandgap (Eg)	Description
FA _{0.83} Cs _{0.17} Pb(I _{0.85} Br _{0.15}) "Cs17Br15"	1.63 eV^{31}	MA-free formamidinium-cesium mixed-halide perovskite composition.
FA _{0.83} Cs _{0.17} Pb(I _{0.75} Br _{0.25}) ₃ "Cs17Br25"	1.70 eV^{22}	Wide bandgap MA-free formamidinium- cesium mixed-halide perovskite composition.
FA _{0.7} Cs _{0.3} PbI ₃	1.52 eV^{41}	Formamidinium-cesium triiodide perovskite composition.
CsPbI ₂ Br	1.92 eV^{42}	Ultra-wide bandgap, all inorganic composition.
MAPbI ₃ "MAPI"	1.59 eV^{43}	Archetypal MAPI perovskite composition.

Table 3.1: List of perovskite compositions, their bandgaps, and a brief description of the composition.

3.3.4 Preparation of Perovskite Films (at Georgia Tech)

In order to screen passivation approaches and to increase overall throughput, we first sought to replicate the $FA_{0.83}Cs_{0.17}Pb(Br_{0.15}I_{0.85})_3$ or "Cs17Br15" perovskite composition selected by our University of Washington (UW) collaborators at Georgia Tech.⁴⁴ Cs17Br15 films were prepared with 5% stoichiometric excess of PbI₂. The structural and optoelectronic properties of Cs17Br15 films have been reported in the literature.³¹ In order to validate the consistency and quality of the films prepared we prepared, we examined their structure by XRD. As shown in Figure 3.17, the diffraction pattern obtained for a film we prepared closely matched with that of a film prepared at UW indicating the crystal structure of the perovskite was consistent.



Figure 3.17: Comparison of XRD analysis of Cs17Br15 films prepared at (a) Georgia Tech and (b) University of Washington. Inset photo in (a) shows the appearance of the perovskite films fabricated at GT.

After verifying the structural consistency of the films, we sought to confirm their photoluminescent properties by measuring the PL lifetime via time-correlated single photon counting (TCSPC). Achieving similar lifetimes allowed us to effectively screen passivators on films and validated the comparable optoelectronic quality of the films. Measurements on a series of control films (unpassivated) fabricated and measured at Georgia Tech exhibited average PL lifetimes almost identical to control films fabricated and measured at UW as shown in Figure 3.18. The PL lifetime of films were measured in the Silva group using a Chimera time correlated single photon counting (TCSPC) instrument. The data was fitted with a stretched exponential.²¹⁻ 22, 31, 45-46



PL Lifetime Comparison

Figure 3.18: PL lifetimes (calculated from stretched exponential fit) of control films fabricated at (a) Georgia Tech. PL lifetimes of control and APTMS passivated films fabricated at UW.

3.3.5 Passivation Screening of Cs17Br15 Perovskite Films (at Georgia Tech)

Once the optoelectronic quality of the control perovskite films was established, a series of screening experiments were carried out. Initially, we examined two series of (neutral) amines. We selected derivatives of APTMS and benzylamine, as both of the parent compounds have been reported as effective passivators for perovskites.^{20, 31} Previously, XPS was used to demonstrate that APTMS acts as both a Lewis base but is also present in a protonated state, whereas the passivation mechanism for benzylamine was not explored experimentally. In addition to the "parent" primary amines, we also explored secondary and tertiary amines with otherwise identical levels of *N*-methylation. We hypothesized that the primary amine functional groups might universally be most effective with a trend of decreasing effectiveness for secondary and tertiary amines due to decreased numbers of hydrogen bond donors. The amines were spin-
coated atop Cs17Br15 films from a 3% v/v solution of amine in chlorobenzene and the passivated films were annealed at 160° C for 5 mins.²⁰



Trends in APTMS derivatives and benzylamine derivatives

Figure 3.19: Time-correlated single photon counting (TCSPC) traces of control and passivated films of Cs17Br15 perovskite with primary, secondary, and tertiary amines. (a-c) Passivation with benzylamine derivatives. (d-f) Passivation with APTMS derivatives.

The data shown in Figure 3.19 suggest two different trends exist for the passivation with amines. Benzylamine-passivated films exhibit a longer lifetime than the *N*-methylbenzylamine-passivated films, which in turn are longer than the lifetimes of the control films. The *N*,*N*-dimethylbenzylamine-passivated film exhibits a decreased lifetime compared to the control film (and to the other primary and secondary benzylamine derivatives). However, derivatives of APTMS clearly do not show the same trend. All films treated with APTMS-derivatives show an increased lifetime compared to their control film counterparts and exhibit longer lifetimes than

benzylamine passivated films. This suggests that the operative passivation mechanism for aminoalkyl-trialkoxysilanes may be different from that for simple amines. Thus, it is likely that the oligomerized siloxane functional group plays a role in passivation.

3.3.6 Passivation on Cs17Br25 Perovskite

Broader screening studies were carried out at the University of Washington and Oxford University. Photoluminescence lifetime measurements from TCSPC were carried out at the University of Washington and photoluminescence quantum yield (PLQY) measurements were carried out at Oxford University.

3.3.6.1 Time-Correlated Single Photon Counting (UW)

The passivators were spin coated atop perovskite films from a 10 mM solution in isopropanol (IPA) or chlorobenzene (CB).



Figure 3.20: TCSPC traces of passivated (orange) and control (blue) films of: (a) BAI, benzylammonium iodide; (b) NBAI, *N*-methyl-benzylammonium iodide; (c) NNBAI, *N*,*N*-dimethyl-benzylammonium iodide; (d) NNNBAI, *N*,*N*-trimethyl-benzylammonium iodide; (e) BABr, benzylammonium bromide; (f) BAOTf, benzylammonium triflate; (g) BAOTs, benzylammonium tosylate; (h) BABF4, benzylammonium tetrafluoroborate; (i) BACl, benzylammonium chloride; (j) CTAB, cetrimonium bromide; (k) Ph₃PS, triphenylphosphine sulfide; (l) TritylSH, triphenylmethanethiol.

Figure 3.20 shows a subset of the molecules screened at the University of Washington. Despite multiple reports of a pronounced passivation effect, including one report of carrier lifetimes exceeding 6 µs, in the literature^{30, 47-48}, the benzylammonium iodide treated film in Fig 3.20 (a) exhibited a shorter lifetime than the control Cs17Br25 film. The remaining benzylammonium iodide derivatives with increasing degree of methylation Fig. 3.20 (b-d) show comparable lifetimes between the control and passivator treated films. Consistent with previous literature reports on other perovskite compositions^{30, 32}, benzylammonium bromide and chloride treated films exhibited increased lifetimes relative to their control counterparts, shown in Fig. 3.20 (e) and (i), respectively. Varying the counterion from halides to triflate, tosylate, and tetrafluoroborate, shown in Fig. 3.20 (e) and (i), respectively, did not show any pronounced passivation effects. In Fig. 3.20 (j), CTAB showed a pronounced passivation effect which was consistent with previous literature reports.⁴⁹⁻⁵⁰ Finally, as shown in Fig. 3.20 (k) and (l), respectively, the Lewis basic triphenylphosphine sulfide showed a very minor improvement to the PL lifetime while triphenylmethanethiol did not improve the lifetime.



Figure 3.21: TCSPC traces of benzylamine passivated (orange) and control (blue) films.

Lastly, the PL lifetime increased most dramatically for the benzylamine passivated film, shown in Figure 3.21. This result is consistent qualitatively with our observations at Georgia Tech, but quantitatively the film shows a much larger passivation effect overall. In summary, varying the counterion within the benzylammonium salts to other halides such as bromide and chloride did exhibit a small passivation effect. Other changes to include pseudohalides and tetrafluoroborate counterions did not demonstrate any passivation effect on this particular composition. Varying the degree of methylation also did not produce any pronounced

passivation effect. Cetrimonium bromide produced the most prominent increases to the lifetime relative to the control film.



3.3.6.2 Photoluminescence Peak Position and Photoluminescence Quantum Yield (Oxford)

Figure 3.22: Photoluminescence properties of control and passivated Cs17Br25 films. (a) PLQY of control and passivated films; (b) Photoluminescence peaks of control and passivated films; (c) Photoluminescence peak positions of control and passivated films.

Figure 3.22 shows a subset of the molecules screened at Oxford on the Cs17Br25 composition. Screening via PLQY provides a slightly easier and more quantitative comparison across a series of samples. The control and IPA treated samples exhibited nearly identical PLQY, verifying that treatment with the carrier solvent for the majority of the passivation agents negligibly changed the PLQY and that any other associated changes must be due to a passivation effect. Amongst the benzylammonium salts, the quaternary ammonium salt, NNNBAI, produced the largest increase in PLQY. The benzylammonium salts with increasing degree of methylation did not produce an increase in the PLQY and, in fact, the PLQY decreased after treatment. The PL spectra in Fig 3.22 (b) were somewhat inconsistent with the PLQY data, perhaps due to etching effects, which can give the appearance of increased PL that is not accounted for in the absence of an integrating sphere.

Amongst the varying counterion series of molecules, only benzylammonium chloride increased the PLQY relative to the control. The pseudohalide and tetrafluoroborate counterions did not produce pronounced changes to the PLQY. Nevertheless, a clear trend can be observed showing the PL peak position shifting towards shorter wavelength with BACl, minimal change with BABr, and a shift towards longer wavelength with BAI. Generally, passivation effects produce an hypsochromic shift because of decreased traps with the bandgap, which increases QFLS. However, depending on the composition of the perovskite, this may be counteracted by the incorporation of halides, which will shift the bandgap and the PL peak position. We observe this effect for the PL position but interestingly do not observe a universal increase in the PLQY.

Notably the neutral amine NNBA produced a pronounced passivation effect, whereas BA and NBA negatively impacted the PLQY. Longer illumination times produced even higher PLQY, under the so called "NNBA-long" label. While this composition is different in that it has a higher bromide content, this result is contradictory to the result obtained at Georgia Tech on Cs17Br15 films—highlighting the sensitive nature of the processing window for these passivation treatments and the difficulty in drawing conclusions from single data points.

3.3.7 Passivation on CsPbI₂Br Perovskite



3.3.7.1 Photoluminescence Peak Position and Photoluminescence Quantum Yield (Oxford)

Figure 3.23: Photoluminescence properties of control and passivated CsPbI₂Br films. (a) PLQY of control and passivated films; (b) Photoluminescence peaks of control and passivated films; (c) Photoluminescence peak positions of control and passivated films.

Figure 3.23 shows a subset of the molecules screened at Oxford on the Cs17Br25 composition. The control and IPA treated samples exhibited very different PLQY, meaning the carrier solvent for the majority of the passivation agents likely also changed the PLQY. It is also noteworthy that a secondary lower energy PL peak appeared around 735 nm which is indicative of halide segregation.

Amongst the benzylammonium salts, benzylammonium tetrafluoroborate showed the most pronounced increase. The PLQY more than doubled, but surprisingly, the PL peak shifted bathochromically. The quaternary ammonium salt, NNNBAI, produced a substantial increase in PLQY. Increasing the degree of methylation in the other benzylammonium iodide salts (secondary and tertiary ammoniums) did not yield any favorable improvement in the PLQY; in fact, the PLQY declined following the treatment. Amongst the varying counterion series of molecules, except for BABF₄, no other surface treatments increased the PLQY relative to the control. The neutral amines did not show a clear trend for the CsPbI₂Br films as BA and NNBA exhibited a passivation effect, while NBA had a detrimental effect on the PLQY.

3.3.8 Passivation on FA0.7Cs0.3PbI3 Perovskite



Figure 3.24: PLQY of control and passivated FA_{0.7}Cs_{0.3}PbI₃ films.

Several passivation treatments were demonstrated to be effective for the FA_{0.7}Cs_{0.3}PbI₃ films. The control and IPA treated films exhibited a marginal difference in PLQY indicating that any increases in PLQY from the passivation treatments could likely be ascribed to the passivation molecule, and not the IPA carrier solvent. The largest improvement in PLQY was observed from the BABr treatment. Similarly, BAI and BACl treatments increased the PLQY, but not the same magnitude. Amongst the non-halide counterions, BABF₄ showed relatively large improvement in the PLQY, whilst BAOTs showed smaller improvements. Interestingly, the benzylammonium triflate was detrimental to the PLQY and etched the film.

The benzylammonium iodide salts with varying degrees of methylation at the ammonium produced varied results. NNBAI significantly improved the PLQY, while the quaternary ammonium compound, NNNBAI, and the secondary ammonium compound, NBAI, both resulted in decreased PLQY. Lastly, the benzylamine treated film showed substantial gains in PLQY relative to the control.



Figure 3.25: PLQY of PMMA-encapsulated FA_{0.7}Cs_{0.3}PbI₃ films (a) before and (b) after aging for 18 hours.

Aging encapsulated films can provide insights into how the passivation treatments influence the stability of the perovskite. For the most part, the initial films exhibited higher PLQY than their unencapsulated counterparts (Fig 3.25). Only the BABr and BABF₄ treated films in Fig. 3.25 (a) exhibited higher PLQY than the control. After aging, the PLQY for all films dropped considerably as shown in Figure 3.25 (b). The smallest loss in PLQY and highest absolute aged-PLQY was observed for the benzylammonium triflate treated half-stack. Most of the passivation treatments showed a dramatic decrease in PLQY after aging, with almost all dropping over an order of magnitude. BABr, BAI, and BAOTs all dropped, but the post-aging PLQY values remained above that of the control.

3.3.9 Solar Cell Device Results

In addition to photoluminescence studies on perovskite films and device "half-stacks", we sought to further explore these materials in full devices. Passivation studies on full device stacks offer more insight into passivation of the perovskite/ C_{60} interface.

Ag C₅₀/BCP Passivation Layer Cs17Br15 MeO-2PACz ITO

3.3.9.1 Primary, Secondary, and Tertiary Benzylammonium Iodides

Figure 3.26: Device architecture and selected benzylammonium iodide passivation materials.

To compare device performance, we focused our analysis on the mixed-cation mixedhalide perovskite, Cs17Br15, which has a bandgap of 1.63 eV.¹⁹ Figure 3.26 shows the p-i-n device architecture used in this study. A self-assembled monolayer of [2-(3,6-dimethoxy-9*H*carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz) was deposited atop ITO as the hole transport layer (HTL).⁵¹ The passivation molecules were dissolved in IPA (10 mM) and dynamically spincoated on the perovskite. C₆₀ and bathocuproine (BCP) were thermally evaporated onto the perovskite layer as the electron transport layer (ETL). Finally, silver (Ag) was thermally evaporated as the top electrode.



Figure 3.27: JV curves of champion devices. Forward (dashed lines) and reverse scans (solid lines) of devices: (blue) control Cs17Br15 device, (orange) BAI passivated device, (green) NBAI passivated device, and (red) NNBAI passivated device.



Figure 3.28: Control and passivated solar cell device figures of merit. (A) Open-circuit voltage, V_{OC}, (B) Power conversion efficiency, PCE, (C) Short-circuit current density, J_{SC}, and (D) Fill factor.

The solar cell devices indicate a pronounced passivation effect for the BAI treated films relative to the control. The V_{OC} , which is closely linked to radiative efficiency of the absorber, increased dramatically on average and to a champion value of 1.18 V. The average and champion fill factors and power conversion efficiencies also increased considerably. A slight decrease in the J_{SC} was observed, possibly due to the insulating properties of the passivation layer and its thickness. The secondary and tertiary ammoniums, NBAI and NNBAI resulted in decreased device performance across the V_{OC}, J_{SC}, and FF.

3.3.9.2 Benzylammonium Sulfonates for Efficient Perovskite Solar Cells



Figure 3.29: Device architecture and selected benzylammonium sulfonate passivation materials. Dipole moments calculated by Dunham Group, Electrical and Computer Engineering Department, University of Washington.

In our analysis of the device performance of benzylamine sulfonate passivators, we studied a wide gap, mixed-cation mixed-halide perovskite, Cs17Br25, which has a bandgap of 1.70 eV.²² Figure 3.29 shows the p-i-n device architecture used in this study. A self-assembled monolayer of [4-(3,6-dimethyl-9*H*-carbazol-9-yl)butyl]phosphonic acid (Me-4PACz) was deposited atop ITO as the hole transport layer (HTL) and a layer of alumina nanoparticles (Al₂O₃) were deposited to increase wettability towards the perovskite solution.⁵²⁻⁵³ The passivation molecules were dissolved in IPA (10 mM) and dynamically spin-coated on the perovskite. C₆₀ and Bathocuproine (BCP) were thermally evaporated onto the perovskite layer as the electron transport layer (ETL). Finally, silver (Ag) was thermally evaporated as the top electrode.



Figure 3.30: J-V curves of (a) control, (b) benzylammonium tosylate (BAOTs), and (c) benzylammonium triflate (BAOTf) champion devices. (d) Statistics for calculated hysteresis index for each device batch.

Solar cell devices fabricated with both passivation molecules show improvements over the control device. The J_{SC} is virtually unchanged, with the most substantial gains in efficiency coming from the fill-factor and V_{OC}. However, BAOTs treated devices show a considerable amount of hysteresis, whereas very minimal hysteresis is observed for the BAOTf treated devices. The pronounced differences in hysteresis are the subject of ongoing investigation.

3.4 Conclusions

A wide variety of candidate passivators were screened across a variety of perovskite compositions. Isolating single variables, as was the original intent of this study, has proven very difficult due to few consistent trends in PL data with structure-property relationships in passivators. Nevertheless, we have successfully identified BAOTf as a highly efficient passivation molecule. Further characterization is necessary and ongoing, but at this time we can note the high efficiency and reduced hysteresis leading to highly efficient wide bandgap, tandem suitable, MA-free perovskite solar cell devices.

Simple PL lifetime or PLQY-based screening studies remain one of the most effective tools to evaluate potential passivation molecules. PLQY may be superior if a 2D perovskite is suspected to have formed. However, PL screening approaches can sometimes fall short if the losses arising from the electron selective or hole-selective contact-induced traps are not accounted for. Likely k_{nr} is relatively slow without the electron-selective fullerene layer, and as such, some screened passivators may not have a substantial effect on neat films. Indeed, in the cases of solar cell devices, the V_{OC} improved dramatically, in contrast to the initial screening studies which didn't necessarily identify these passivation materials. Additionally, these experiments are highly sensitive to a huge number of variables. Control films must be of a sufficiently high optoelectronic quality (relatively defect free which can be influenced considerably by the quality of the precursors), stoichiometric excess of inorganics or organics must be carefully considered, and the effects of aging should not be ruled out. Lastly, certain passivation approaches should not always be considered innocent, and the subject of the reactivity of various amines with other perovskite constituents will be explored in further detail in the subsequent chapter.

3.5 References

1. Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T., Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131* (17), 6050-6051.

2. Park, N.-G., Perovskite solar cells: an emerging photovoltaic technology. *Mater. Today* **2015**, *18* (2), 65-72.

3. Snaith, H. J., Present status and future prospects of perovskite photovoltaics. *Nature Materials* **2018**, *17* (5), 372-376.

4. Jena, A. K.; Kulkarni, A.; Miyasaka, T., Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chem. Rev.* **2019**, *119* (5), 3036-3103.

5. Mitzi, D. B., Introduction: Perovskites. *Chem. Rev.* **2019**, *119* (5), 3033-3035.

6. Faridi, A. W.; Imran, M.; Tariq, G. H.; Ullah, S.; Noor, S. F.; Ansar, S.; Sher, F., Synthesis and Characterization of High-Efficiency Halide Perovskite Nanomaterials for Light-Absorbing Applications. *Industrial & Engineering Chemistry Research* **2023**, *62* (11), 4494-4502.

7. Miyata, A.; Mitioglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J., Direct measurement of the exciton binding energy and effective masses for charge carriers in organic–inorganic tri-halide perovskites. *Nature Physics* **2015**, *11* (7), 582-587.

8. Adhyaksa, G. W. P.; Veldhuizen, L. W.; Kuang, Y.; Brittman, S.; Schropp, R. E. I.; Garnett, E. C., Carrier Diffusion Lengths in Hybrid Perovskites: Processing, Composition, Aging, and Surface Passivation Effects. *Chem. Mater.* **2016**, *28* (15), 5259-5263.

9. De Wolf, S.; Holovsky, J.; Moon, S.-J.; Löper, P.; Niesen, B.; Ledinsky, M.; Haug, F.-J.; Yum, J.-H.; Ballif, C., Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. *The Journal of Physical Chemistry Letters* **2014**, *5* (6), 1035-1039.

10. Oliver, R. D. J.; Caprioglio, P.; Peña-Camargo, F.; Buizza, L. R. V.; Zu, F.; Ramadan, A. J.; Motti, S. G.; Mahesh, S.; McCarthy, M. M.; Warby, J. H.; Lin, Y.-H.; Koch, N.; Albrecht, S.; Herz, L. M.; Johnston, M. B.; Neher, D.; Stolterfoht, M.; Snaith, H. J., Understanding and suppressing non-radiative losses in methylammonium-free wide-bandgap perovskite solar cells. *Energy & Environmental Science* **2022**, *15* (2), 714-726.

11. McCluskey, M. D.; Janotti, A., Defects in Semiconductors. J. Appl. Phys. 2020, 127 (19), 190401.

12. Kim, G.-W.; Petrozza, A., Defect Tolerance and Intolerance in Metal-Halide Perovskites. *Adv. Energy Mater.* **2020**, *10* (37), 2001959.

13. Bera, S.; Saha, A.; Mondal, S.; Biswas, A.; Mallick, S.; Chatterjee, R.; Roy, S., Review of defect engineering in perovskites for photovoltaic application. *Materials Advances* **2022**, *3* (13), 5234-5247.

14. Pradhan, R. R.; Eswaran, M. K.; Subbiah, A. S.; Babayigit, A.; De Wolf, S.; Schwingenschlögl, U., Elucidating the Role of Contact-Induced Gap States and Passivation Molecules at Perovskite/Metal Contacts. *ACS Applied Energy Materials* **2023**, *6* (8), 4111-4118.

15. Warby, J.; Zu, F.; Zeiske, S.; Gutierrez-Partida, E.; Frohloff, L.; Kahmann, S.; Frohna, K.; Mosconi, E.; Radicchi, E.; Lang, F.; Shah, S.; Peña-Camargo, F.; Hempel, H.; Unold, T.; Koch, N.; Armin, A.; De Angelis, F.; Stranks, S. D.; Neher, D.; Stolterfoht, M., Understanding Performance Limiting Interfacial Recombination in pin Perovskite Solar Cells. *Adv. Energy Mater.* **2022**, *12* (12), 2103567.

16. Ye, J.; Byranvand, M. M.; Martínez, C. O.; Hoye, R. L. Z.; Saliba, M.; Polavarapu, L., Defect Passivation in Lead-Halide Perovskite Nanocrystals and Thin Films: Toward Efficient LEDs and Solar Cells. *Angew. Chem. Int. Ed.* **2021**, *60* (40), 21636-21660.

17. Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J., Surface passivation of perovskite film for efficient solar cells. *Nature Photonics* **2019**, *13* (7), 460-466.

18. Perini, C. A. R.; Rojas-Gatjens, E.; Ravello, M.; Castro-Mendez, A.-F.; Hidalgo, J.; An, Y.; Kim, S.; Lai, B.; Li, R.; Silva-Acuña, C.; Correa-Baena, J.-P., Interface Reconstruction from Ruddlesden–Popper Structures Impacts Stability in Lead Halide Perovskite Solar Cells. *Adv. Mater.* **2022**, *34* (51), 2204726.

19. Cho, Y.; Soufiani, A. M.; Yun, J. S.; Kim, J.; Lee, D. S.; Seidel, J.; Deng, X.; Green, M. A.; Huang, S.; Ho-Baillie, A. W. Y., Mixed 3D–2D Passivation Treatment for Mixed-Cation Lead Mixed-Halide Perovskite Solar Cells for Higher Efficiency and Better Stability. *Adv. Energy Mater.* **2018**, *8* (20), 1703392.

20. Wang, F.; Geng, W.; Zhou, Y.; Fang, H.-H.; Tong, C.-J.; Loi, M. A.; Liu, L.-M.; Zhao, N., Phenylalkylamine Passivation of Organolead Halide Perovskites Enabling High-Efficiency and Air-Stable Photovoltaic Cells. *Adv. Mater.* **2016**, *28* (45), 9986-9992.

21. Shi, Y.; Rojas-Gatjens, E.; Wang, J.; Pothoof, J.; Giridharagopal, R.; Ho, K.; Jiang, F.; Taddei, M.; Yang, Z.; Sanehira, E. M.; Irwin, M. D.; Silva-Acuña, C.; Ginger, D. S., (3-Aminopropyl)trimethoxysilane Surface Passivation Improves Perovskite Solar Cell Performance by Reducing Surface Recombination Velocity. *ACS Energy Letters* **2022**, *7* (11), 4081-4088.

22. Taddei, M.; Smith, J. A.; Gallant, B. M.; Zhou, S.; Westbrook, R. J. E.; Shi, Y.; Wang, J.; Drysdale, J. N.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Snaith, H. J.; Ginger, D. S., Ethylenediamine Addition Improves Performance and Suppresses Phase Instabilities in Mixed-Halide Perovskites. *ACS Energy Letters* **2022**, 4265-4273.

23. Jiang, Q.; Tong, J.; Xian, Y.; Kerner, R. A.; Dunfield, S. P.; Xiao, C.; Scheidt, R. A.; Kuciauskas, D.; Wang, X.; Hautzinger, M. P.; Tirawat, R.; Beard, M. C.; Fenning, D. P.; Berry, J. J.; Larson, B. W.; Yan, Y.; Zhu, K., Surface reaction for efficient and stable inverted perovskite solar cells. *Nature* **2022**, *611* (7935), 278-283.

24. Noel, N. K.; Abate, A.; Stranks, S. D.; Parrott, E. S.; Burlakov, V. M.; Goriely, A.; Snaith, H. J., Enhanced Photoluminescence and Solar Cell Performance via Lewis Base Passivation of Organic–Inorganic Lead Halide Perovskites. *ACS Nano* **2014**, *8* (10), 9815-9821.

25. Abate, A.; Saliba, M.; Hollman, D. J.; Stranks, S. D.; Wojciechowski, K.; Avolio, R.; Grancini, G.; Petrozza, A.; Snaith, H. J., Supramolecular Halogen Bond Passivation of Organic– Inorganic Halide Perovskite Solar Cells. *Nano Lett.* **2014**, *14* (6), 3247-3254.

26. Akman, E.; Shalan, A. E.; Sadegh, F.; Akin, S., Moisture-Resistant FAPbI3 Perovskite Solar Cell with 22.25 % Power Conversion Efficiency through Pentafluorobenzyl Phosphonic Acid Passivation. *ChemSusChem* **2021**, *14* (4), 1176-1183.

27. Yang, S.; Dai, J.; Yu, Z.; Shao, Y.; Zhou, Y.; Xiao, X.; Zeng, X. C.; Huang, J., Tailoring Passivation Molecular Structures for Extremely Small Open-Circuit Voltage Loss in Perovskite Solar Cells. *J. Am. Chem. Soc.* **2019**, *141* (14), 5781-5787.

28. Lee, S.-H.; Jeong, S.; Seo, S.; Shin, H.; Ma, C.; Park, N.-G., Acid Dissociation Constant: A Criterion for Selecting Passivation Agents in Perovskite Solar Cells. *ACS Energy Letters* **2021**, *6* (4), 1612-1621.

29. Park, S. M.; Wei, M.; Xu, J.; Atapattu, H. R.; Eickemeyer, F. T.; Darabi, K.; Grater, L.; Yang, Y.; Liu, C.; Teale, S.; Chen, B.; Chen, H.; Wang, T.; Zeng, L.; Maxwell, A.; Wang, Z.; Rao,

K. R.; Cai, Z.; Zakeeruddin, S. M.; Pham, J. T.; Risko, C. M.; Amassian, A.; Kanatzidis, M. G.; Graham, K. R.; Grätzel, M.; Sargent, E. H., Engineering ligand reactivity enables high-temperature operation of stable perovskite solar cells. *Science* **2023**, *381* (6654), 209-215.

30. Chen, H.-C.; Lan, J.-M.; Hsu, H.-L.; Li, C.-W.; Shieh, T.-S.; Wong, K.-T.; Chen, C.-P., Synergistic improvements in the performance and stability of inverted planar MAPbI3-based perovskite solar cells incorporating benzylammonium halide salt additives. *Materials Chemistry Frontiers* **2021**, *5* (8), 3378-3387.

31. Jariwala, S.; Burke, S.; Dunfield, S.; Shallcross, R. C.; Taddei, M.; Wang, J.; Eperon, G. E.; Armstrong, N. R.; Berry, J. J.; Ginger, D. S., Reducing Surface Recombination Velocity of Methylammonium-Free Mixed-Cation Mixed-Halide Perovskites via Surface Passivation. *Chem. Mater.* **2021**, *33* (13), 5035-5044.

32. Oliver, R. D. J.; Lin, Y.-H.; Horn, A. J.; Xia, C. Q.; Warby, J. H.; Johnston, M. B.; Ramadan, A. J.; Snaith, H. J., Thermally Stable Passivation toward High Efficiency Inverted Perovskite Solar Cells. *ACS Energy Letters* **2020**, *5* (11), 3336-3343.

33. Alanazi, A. Q.; Almalki, M. H.; Mishra, A.; Kubicki, D. J.; Wang, Z.; Merten, L.; Eickemeyer, F. T.; Zhang, H.; Ren, D.; Alyamani, A. Y.; Albrithen, H.; Albadri, A.; Alotaibi, M. H.; Hinderhofer, A.; Zakeeruddin, S. M.; Schreiber, F.; Hagfeldt, A.; Emsley, L.; Milić, J. V.; Graetzel, M., Benzylammonium - Mediated Formamidinium Lead Iodide Perovskite Phase Stabilization for Photovoltaics. *Adv. Funct. Mater.* **2021**, *31* (30).

34. Tan, S.; Huang, T.; Yavuz, I.; Wang, R.; Weber, M. H.; Zhao, Y.; Abdelsamie, M.; Liao, M. E.; Wang, H.-C.; Huynh, K.; Wei, K.-H.; Xue, J.; Babbe, F.; Goorsky, M. S.; Lee, J.-W.; Sutter-Fella, C. M.; Yang, Y., Surface Reconstruction of Halide Perovskites During Post-treatment. *J. Am. Chem. Soc.* **2021**, *143* (18), 6781-6786.

35. Smith, I. C.; Hoke, E. T.; Solis-Ibarra, D.; McGehee, M. D.; Karunadasa, H. I., A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability. *Angew. Chem. Int. Ed.* **2014**, *53* (42), 11232-11235.

36. Mohanty, A. D.; Bae, C., Mechanistic analysis of ammonium cation stability for alkaline exchange membrane fuel cells. *Journal of Materials Chemistry A* **2014**, *2* (41), 17314-17320.

37. Gibson, H. W.; Jones, J. W.; Zakharov, L. N.; Rheingold, A. L.; Slebodnick, C., Complexation Equilibria Involving Salts in Non-Aqueous Solvents: Ion Pairing and Activity Considerations. *Chemistry – A European Journal* **2011**, *17* (11), 3192-3206.

38. Conings, B.; Drijkoningen, J.; Gauquelin, N.; Babayigit, A.; D'Haen, J.; D'Olieslaeger, L.; Ethirajan, A.; Verbeeck, J.; Manca, J.; Mosconi, E.; Angelis, F. D.; Boyen, H.-G., Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite. *Adv. Energy Mater.* **2015**, *5* (15), 1500477.

39. Mahesh, S.; Ball, J. M.; Oliver, R. D. J.; McMeekin, D. P.; Nayak, P. K.; Johnston, M. B.; Snaith, H. J., Revealing the origin of voltage loss in mixed-halide perovskite solar cells. *Energy & Environmental Science* **2020**, *13* (1), 258-267.

40. Peña-Camargo, F.; Caprioglio, P.; Zu, F.; Gutierrez-Partida, E.; Wolff, C. M.; Brinkmann, K.; Albrecht, S.; Riedl, T.; Koch, N.; Neher, D.; Stolterfoht, M., Halide Segregation versus Interfacial Recombination in Bromide-Rich Wide-Gap Perovskite Solar Cells. *ACS Energy Letters* **2020**, *5* (8), 2728-2736.

41. Xia, X.; Wu, W.; Li, H.; Zheng, B.; Xue, Y.; Xu, J.; Zhang, D.; Gao, C.; Liu, X., Spray reaction prepared FA1–xCsxPbI3 solid solution as a light harvester for perovskite solar cells with improved humidity stability. *RSC Advances* **2016**, *6* (18), 14792-14798.

42. Sutton, R. J.; Eperon, G. E.; Miranda, L.; Parrott, E. S.; Kamino, B. A.; Patel, J. B.; Hörantner, M. T.; Johnston, M. B.; Haghighirad, A. A.; Moore, D. T.; Snaith, H. J., Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. *Adv. Energy Mater.* **2016**, *6* (8), 1502458.

43. Tao, S.; Schmidt, I.; Brocks, G.; Jiang, J.; Tranca, I.; Meerholz, K.; Olthof, S., Absolute energy level positions in tin- and lead-based halide perovskites. *Nature Communications* **2019**, *10* (1), 2560.

44. Kim, J.; Saidaminov, M. I.; Tan, H.; Zhao, Y.; Kim, Y.; Choi, J.; Jo, J. W.; Fan, J.; Quintero-Bermudez, R.; Yang, Z.; Quan, L. N.; Wei, M.; Voznyy, O.; Sargent, E. H., Amide-Catalyzed Phase-Selective Crystallization Reduces Defect Density in Wide-Bandgap Perovskites. *Adv. Mater.* **2018**, *30* (13), 1706275.

45. Jariwala, S.; Sun, H.; Adhyaksa, G. W. P.; Lof, A.; Muscarella, L. A.; Ehrler, B.; Garnett, E. C.; Ginger, D. S., Local Crystal Misorientation Influences Non-radiative Recombination in Halide Perovskites. *Joule* **2019**, *3* (12), 3048-3060.

46. Wang, J.; Fu, W.; Jariwala, S.; Sinha, I.; Jen, A. K. Y.; Ginger, D. S., Reducing Surface Recombination Velocities at the Electrical Contacts Will Improve Perovskite Photovoltaics. *ACS Energy Letters* **2019**, *4* (1), 222-227.

47. Alanazi, A. Q.; Almalki, M. H.; Mishra, A.; Kubicki, D. J.; Wang, Z.; Merten, L.; Eickemeyer, F. T.; Zhang, H.; Ren, D.; Alyamani, A. Y.; Albrithen, H.; Albadri, A.; Alotaibi, M. H.; Hinderhofer, A.; Zakeeruddin, S. M.; Schreiber, F.; Hagfeldt, A.; Emsley, L.; Milić, J. V.; Graetzel, M., Benzylammonium-Mediated Formamidinium Lead Iodide Perovskite Phase Stabilization for Photovoltaics. *Adv. Funct. Mater.* **2021**, *31* (30), 2101163.

48. Yang, X.; Fu, Y.; Su, R.; Zheng, Y.; Zhang, Y.; Yang, W.; Yu, M.; Chen, P.; Wang, Y.; Wu, J.; Luo, D.; Tu, Y.; Zhao, L.; Gong, Q.; Zhu, R., Superior Carrier Lifetimes Exceeding 6 μs in Polycrystalline Halide Perovskites. *Adv. Mater.* **2020**, *32* (39), 2002585.

49. Guo, Y.; Li, X.; Kang, L.; Cheng, C.; He, X.; Liu, X.; Liu, J.; Li, Y.; Dong, C., Mechanistic Understanding of Cetyltrimethylammonium Bromide-Assisted Durable CH3NH3PbI3 Film for Stable ZnO-Based Perovskite Solar Cells. *ACS Applied Energy Materials* **2020**, *3* (10), 9856-9865. 50. Wang, S.; Zhu, Y.; Wang, C.; Ma, R., Interface modification by a multifunctional ammonium salt for high performance and stable planar perovskite solar cells. *Journal of Materials Chemistry A* **2019**, *7* (19), 11867-11876.

51. Al-Ashouri, A.; Magomedov, A.; Roß, M.; Jošt, M.; Talaikis, M.; Chistiakova, G.; Bertram, T.; Márquez, J. A.; Köhnen, E.; Kasparavičius, E.; Levcenco, S.; Gil-Escrig, L.; Hages, C. J.; Schlatmann, R.; Rech, B.; Malinauskas, T.; Unold, T.; Kaufmann, C. A.; Korte, L.; Niaura, G.; Getautis, V.; Albrecht, S., Conformal monolayer contacts with lossless interfaces for perovskite single junction and monolithic tandem solar cells. *Energy & Environmental Science* **2019**, *12* (11), 3356-3369.

52. Al-Ashouri, A.; Köhnen, E.; Li, B.; Magomedov, A.; Hempel, H.; Caprioglio, P.; Márquez, J. A.; Morales Vilches, A. B.; Kasparavicius, E.; Smith, J. A.; Phung, N.; Menzel, D.; Grischek, M.; Kegelmann, L.; Skroblin, D.; Gollwitzer, C.; Malinauskas, T.; Jošt, M.; Matič, G.; Rech, B.; Schlatmann, R.; Topič, M.; Korte, L.; Abate, A.; Stannowski, B.; Neher, D.; Stolterfoht, M.; Unold, T.; Getautis, V.; Albrecht, S., Monolithic perovskite/silicon tandem solar cell with >29% efficiency by enhanced hole extraction. *Science* **2020**, *370* (6522), 1300-1309.

53. Schultes, M.; Giesbrecht, N.; Küffner, J.; Ahlswede, E.; Docampo, P.; Bein, T.; Powalla, M., Universal Nanoparticle Wetting Agent for Upscaling Perovskite Solar Cells. *ACS Applied Materials & Interfaces* **2019**, *11* (13), 12948-12957.

4 Exploring the Reactivity of Amines and Formamidinium Cations in Perovskite Inks



Figure 4.1: Graphical abstract demonstrating transamination reactions possible in perovskite precursor solutions.

This project was a collaboration with Margherita Taddei, Joel Smith, Benjamin Gallant, Suer Zhou, Robert J. E. Westbrook, Yangwei Shi, Jian Wang, James Drysdale, Junxiang Zhang, and Pattarawadee Therdkatanyuphong. Margherita Taddei prepared FA_{0.83}Cs_{0.17}Pb(I_{0.75}Br_{0.25})₃ films and performed XRD, TRPL spectroscopy, hyperspectral PL, and ToF-SIMs measurements. Junxiang Zhang prepared mono- and bis-substituted benzylformamidinium iodide compounds.

This work was supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technology Office (SETO), Award Number DE-EE0008747, and the Office of Naval Research (ONR), Award Number N00014-20-1-2587. I also wish to acknowledge support of this project by the Department of Education Graduate Assistance in Areas of National Need (GAANN) program at Georgia Institute of Technology (Award #P200A180075).

4.1 Introduction

As discussed in Chapter 1, metal-halide perovskites have rapidly come to prominence over the last decade for their remarkable optoelectronic properties.¹⁻² These properties have enabled their application in various optoelectronic devices including photodetectors, LEDs, and solar cells. More complex approaches for the processing of lead-halide perovskites (LHPs) have evolved as devices incorporating these materials have increased in efficiency. Recently, precursor solution aging, the use of various additives, and certain passivation approaches have been revealed to lead to unintended chemical reactions which are sometimes overlooked.

Several previous studies have examined the reaction chemistry that can take place in perovskite inks. One study identified the transamidation reaction between the common processing solvent *N*,*N*-dimethylformamide (DMF), and methylamine which results in dimethylammonium halide incorporation into films.³ Dou et al. used time-of-flight secondary ion mass spectrometry (ToF-SIMS) to confirm the transamidation reaction with DMF upon aging the widely used triple cation perovskite composition reported by Saliba et al.⁴⁻⁵ Subsequent studies utilized dimethylammonium halide additives to tune the bandgap, improve crystallization, and improve solar cell device performance.⁶⁻⁸

Van Gompel et al. identified trace quantities of ammonium iodide (NH₄I) in commercial formamidinium iodide (FAI) and the potential for FAI to degrade to ammonium iodide (NH₄I) to form ammonium lead iodide (NH₄PbI₃) in acidic precursor solutions.⁹ Reactions of PbI₂ with amines have been identified in the literature. Researchers have demonstrated that degradation of alkylammonium lead halide perovskites to Pb⁰ can occur in perovskite precursor solutions¹⁰⁻¹¹ as well as in films in the dark and under irradiation.¹² Others have identified *N*-formylation

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reactions between amine additives in perovskite precursor solutions, which was suggested to be initiated via acidic hydrolysis of DMF.¹³

Others have reported the reaction of FA⁺ and MA⁺ in aged mixed-cation perovskite precursors to form *N*-methylformamidinium (MFA⁺) or *N*,*N*'-dimethylformamidinium (DMFA⁺) cations and ammonium halide.¹⁴⁻¹⁶ Valenzano et al. observed the same reaction, although noted that the presence of Cs⁺ slowed the exchange kinetics.¹⁷ Some impurities such as trace acetate or lead oxide contained in the perovskite precursors were found to catalyze the exchange reaction in mixed cation perovskite inks.¹⁸ Trace triiodide (I₃⁻) was found to catalyze degradation of MA⁺ and FA⁺ perovskites via deprotonation, where formamidine can decompose rapidly.¹⁹

Recently, amine and ammonium additives and surface passivators have become more prominent and the potential for a *transimination* reaction with amines other than MA has been identified. A surface transimination reaction with FA⁺ was identified to take place upon deposition of 3-(aminomethyl)pyridine (3-APy) atop perovskite thin films allowing for very high solar cell device perfomance.²⁰ Very recently, the ubiquitous surface passivators phenyethylammonium (PEA⁺) and butylammonium (BA⁺) were found to undergo deprotonation followed by transimination reaction with FA⁺ in perovskite films.²¹

In Chapter 3, I discussed a variety of passivators. Several passivators contained neutral amine functional groups. In contrast to a post-perovskite growth deposition, a related passivation approach involves the addition of a passivation agent in the precursor solution. Our collaborators at the University of Washington (UW) and Oxford University adapted an approach using ethylene diamine (EDA) to widen the bandgap of the resulting "hollow" perovskite²² in the mixed-cation mixed-halide (Cs17Br25) perovskite composition for silicon-perovskite tandems. They also explore passivation with benzylamine addition to the precursor solution.

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Consequently, we explored the reactivity of amines and ammoniums with formamidinium salts and built upon our accumulated knowledge of their solution chemistry to synthesize and utilize product(s) formed in these reactions as additives and surface passivation agents in perovskites. This work helps to elucidate the role of the amine/ammonium additives in controlling FA-containing perovskite growth and crystallization processes.

4.2 Experimental

General

All chemicals were purchased from commercial sources and used as received unless stated otherwise. Column chromatography was carried out using silica gel (46-63 μ m, Sorbent) as the stationary phase, and thin-layer chromatography (TLC) was performed on precoated silica-gel plates (0.25 mm thick, 60F254, EMD, Germany) and visualized under UV light. Nuclear magnetic spectroscopy measurements were carried out on Bruker Avance III 400 or Avance III HD 500 MHz instruments and calibrated using the solvent residual as an internal reference (DMSO, 2.50 ppm ¹H NMR).

Materials:

Lead bromide (PbBr₂, 99.998% metals basis), and cesium iodide (CsI, 99.999% metal basis) were purchased from Alfa Aesar. Lead iodide (PbI₂, perovskite grade) was purchased from Tokyo Chemical Industries ltd. Formamidinium iodide (FAI, >99.99%) and methylammonium iodide (MAI, >99.99%) were purchased from Great Cell Solar. Ethylenediamine (puriss. p. a., absolute \geq 99.5%), ethane-1,2-diammonium iodide (EDAH₂I₂), ethane-1,2-diammonium bromide (EDAH₂Br₂), lead acetate trihydrate (99.999% trace metals basis), dimethylformamide (DMF, anhydrous), dimethyl sulfoxide (DMSO, anhydrous), and anisole (anhydrous) were purchased from Sigma-Aldrich. Synthesis:

The synthesis of $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ thin films was all conducted inside a N₂ filled glovebox. The FA_{0.83}Cs_{0.17}Pb(I_{0.75}Br_{0.25})₃ precursor solutions of 1.2M were prepared dissolving 0.75 mmol of PbI₂, 0.45 mmol of PbBr₂,0.204 mmol of CsI and 0.996 mmol of FAI in 0.8 mL DMF and 0.2 mL of DMSO. Solutions of 1.45M were prepared mixing 0.9 mmol of PbI₂, 0.54 mmol of PbBr₂, 0.25 mmol of CsI and 1.204 mmol of FAI in 0.8 mL DMF and 0.2 mL DMSO. All the solutions were stirred overnight at 600 rpm. After stirring, the solutions were filtered with a 0.2 µm PTFE filter. Ethylenediamine (EDA) was added to the precursor solution after overnight stirring in molar percentages of 1, 10, 20, 40 (density = 0.899 g/mL). Solutions were deposited after a few hours following EDA addition. Glass substates $(2.5 \times 2.5 \text{ cm})$ were cleaned through a sequential sonication of 10 minutes in soap solution, deionized water, acetone, and isopropanol (IPA). Cleaned glass substrates were ozone cleaned for 30 min before spin coating. The precursor solution (80 µL) was deposited on the glass substrates and spin coated for 10 s at 1000 rpm (200 rpm/s) and 35 s at 5000 rpm (800 rpm/s). Anisole (Sigma Aldrich) was used as antisolvent and dropped (330 μ L) after 40 s. Anisole was filtered using a 0.45 μ m PTFE filter before usage. The films were annealed at 100 °C for 45 min. Then the films were stored under N2 in the dark. Films were encapsulated with a glass substrate (2.5 x 2.5 cm) using a 2-part epoxy resin-polymercaptan glue (Epoxy Adhesive C-POXY 30 by CECCORP) mixed in ratio 1:1. Encapsulation was performed inside the glove box. Encapsulated films were left inside the glove box overnight before characterization.

Time Resolved Photoluminescence:

The TRPL spectra at 405 nm excitation were acquired using an Edinburgh FLS1000 spectrometer with EPL-405, a 405 nm picosecond pulsed diode laser. The repetition rate is

controlled by an internal trigger input and was set to 1 MHz. The emission and excitation slits were controlled to have an emission signal frequency of 1 to 2% of the start rate. The slits were kept constant for all the measurements and the film stage was moved in the x direction to maximize the emission. A PMT-900 detector was used in time-correlated single photon counting (TCSPC) mode with an instrumental response width of approximately 600 ps.

Hyperspectral microscope:

Hyperspectral measurements were performed using a Photon etc. IMA upright microscope fitted with a transmitted darkfield condenser and a 60X objective (Nikon Plan RT, NA 0.7, CC 0-1.2). The excitation was done using a mercury halide lamp (Nikon ultrahigh pressure 130 W mercury lamp) passing through a 500 nm short-pass filter and emission was collected through a 500 dichroic filter and 550 nm long-pass filter. The lamp has six levels of light intensity, and all the measurements were taken using the lowest intensity (ND32) with total incident power on the sample of 256 μ W. The Hyperspectral Microscope uses a tunable Bragg filter to image a sample at specific wavelengths. The sample is imaged throughout the spectral range and these images are combined into a single "Hyper Cube", which carries spectral information at each pixel. This allows for diffraction limited imaging, rather than being constrained by the spot size of the fiber optic cable. Post-processing was done in the proprietary Photon etc. PHySpec Software.

X-ray Diffraction:

XRD patterns were obtained using a Bruker D8 Discover with I μ S 2-D XRD System (Cu K α radiation at 50 W). Powder XRD patterns and structural views were calculated and rendered using VESTA.³

ToF-SIMS:

ToF-SIMS spectra were acquired on a IONTOF TOF.SIMS5 spectrometer using a 25 keV Bi³⁺ cluster ion source in the pulsed mode. Spectra were acquired for both positive and negative secondary ions over a mass range of m/z = 0 to 800. The ion source was operated with at a current of 0.09 pA and spectra were acquired using an analysis area of 200 µm x 200 µm using 256 x 256 pixels.

Reagent Synthesis:

$$\begin{array}{c} -N \\ 0 \\ 0 \\ \end{array} \\ 0 \\ \end{array} \\ \begin{array}{c} H_2 N \\ \hline N \\ H_2 \\ \hline N \\ PhMe \\ 80^{\circ}C, 24hrs \\ \end{array} \\ \begin{array}{c} NH_2 \\ N \\ \end{array} \\ \begin{array}{c} NH_2 \\ N \\ \end{array}$$

Figure 4.2: Synthesis of 4,5-dihydroimidazole (imidazoline).

4,5-dihydroimidazole (imidazoline), was synthesized according to a modified literature procedure.²³ An oven-dried three-neck 100mL round-bottomed flask was equipped with a stir bar and air condenser and purged and refilled with nitrogen three times. 50 mL of anhydrous toluene was added via cannula. Dry ethylene diamine (6.82 mL, 64.8 mmol) and technical grade dimethylformamide diacetal (4.13mL, 61.7 mmol) were added sequentially added via syringe. The reaction was heated at 80°C for 72 hrs. The solvent was removed under reduced pressure and the product was purified by either Kugelrohr short-path distillation or vacuum distillation. A white, hygroscopic, waxy solid was obtained in low yield. 1.18 g (27%). ¹H NMR (400 MHz, CD₃CN) δ 6.95 (s, 1H), 3.41 (d, *J* = 1.1 Hz, 4H). ¹H NMR (400 MHz, CDCl₃) δ 7.10 – 7.05 (m, 1H), 4.75 (s, 1H), 3.75 (s, 2H), 3.35 (s, 2H).



Figure 4.3: ¹H NMR (400 MHz, CD₃CN).



Figure 4.4: ¹H NMR (400 MHz, CDCl3).

4.3 **Results and Discussion**

4.3.1 Scope of Amines and Ammoniums in Perovskite Inks



Figure 4.5: Selected passivation agents and solution additives in perovskite solar cells. From left to right: phenethylammonium bromide (PEABr), dimethylammonium chloride (DMACl), and (3-aminopropyl)trimethoxysilane (APTMS).

Considering our initial findings with ethylene diamine and benzylamine, we sought to explore the reactivity of alternative passivation agents and solution additives. We suspected that treatments utilizing protonated ammonium species would be less likely to react with FAI in solution. Nevertheless, we wanted to thoroughly examine the reactivity of both amines and ammoniums. Specifically, we checked the reactivity of a primary ammonium, phenethylammonium bromide (PEABr), a secondary ammonium, dimethylammonium chloride (DMACl), and another primary amine, (3-aminopropyl)trimethoxysilane (APTMS).

Phenethylammonium derivatives, including PEABr, are amongst the most widely used passivation treatments in PSCs in the literature and have produced very efficient cells.²⁴⁻²⁶ Dimethylammonium chloride has been extensively studied as an additive in perovskite inks.⁶⁻⁸ (3-Aminopropyl)trimethoxysilane (APTMS) was briefly introduced in Chapter 3 (with other silanes of varying N-methylation) as a passivation agent and has been used in the literature to achieve very small surface recombination velocities and good solar cell performance *via* both solution and vapor deposition methods.²⁷⁻²⁸

4.3.2 Nuclear Magnetic Resonance (NMR) Solution Studies

4.3.2.1 Screening Reactivity of Amines and Ammoniums

We examined the reactivity of the additives via comixing the amine/ammonium and FAI in equimolar amounts (~0.1M) in DMSO- d_6 . We monitored the reactions by ¹H-NMR spectroscopy at times of 0, 2, 4, 6, 8, and 24 hours. The integrals were normalized using the residual DMSO proton resonance.



Figure 4.6: ¹H-NMR spectra of the initial mixture of PEABr and FAI in DMSO-d₆ at T_{0h} (bottom) and at T_{24h} (top) in DMSO-d₆. The arrow in the top spectrum indicates possible formamidinium C-H peak of mono-subsituted phenethylammonium-formamidinium.

We first examined the reaction of PEABr and FAI. The initial (bottom) and final spectra

(top, after 24 hours) are shown above in Figure 4.6. We can see that the spectra do not change

considerably after allowing the solution to react for 24 hours—even after 2hours the spectra are nearly identical. Only a very small amount of what appears to be the mono-substituted phenethylammonium-formamidinium is observed. The integral can be used to roughly quantitate the amount of mono-substituted product at ~4%.



Figure 4.7: ¹H-NMR spectra of the initial mixture of DMACl and FAI in DMSO-d6 at T_{0h} (bottom) and at T_{24h} (top).

Next, we examined the reactivity of DMACl and FAI in DMSO- d_6 . The initial (bottom) and final spectra (top, after 24 hours) are shown above in Figure 4.7. We can see that the spectra do not change considerably after allowing the solution to react for 24 hours—even after 2 hours

the spectra are nearly identical. Unfortunately, the N-CH₃ protons of dimethylammonium are mostly obstructed by the residual water signal. The most significant change in the spectra is likely due to the N-H proton exchange. Two very small (below limit-of-quantitation (LOQ)) peaks are observed at 2.98 and 3.18 ppm which could indicate the formation of an extremely small amount of the mono-substituted dimethylammonium-formamidinium.



Figure 4.8: ¹H-NMR spectra of FAI (bottom), a mixture of APTMS and FAI (middle), and APTMS (top). The blue highlights indicate peaks attributed to the mono-APTMS-FA-adduct.

Unlike the ammonium species discussed above, the neutral APTMS undergoes rapid chemical transimidation as evidenced by ¹H-NMR spectroscopy shown in Figure 4.8. Several reactions are likely taking place. Proton transfer reactions take place to protonate the APTMS to

some extent, accounted for, in part, by the N-H proton at 5.03 ppm (this peak can shift considerably, likely due to the resonance representing an average NH/OH peak due to rapid proton exchange with residual H_2O). Consistent with our observations in the case of ethylene diamine and benzylamine, we can observe the formation of the mono-substituted APTMS-FAI adduct from the peaks highlighted in blue. Specifically, we see two new peaks that likely correspond to the *E* and *Z* isomers of the mono-substituted APTMS-FAI at 7.85 and 7.70 ppm. We also can observe the formation of a new peak 3.47 ppm, likely corresponding to the aliphatic CH₂ protons that are adjacent to the FA-adduct NH. The integration in the downfield region (near 7.5 ppm) indicates the formation of two isomers of the mono-transiminated product. This analysis is consistent with other unreported data from our group on the isomers of monotransiminated FAI with benzylamine.





Overall, neutral amines react rapidly and form appreciable amounts of transiminated products (on timescales more quickly than an NMR spectrum can be measured). In contrast, it appears that the protonated ammonium species do not appreciably react with FA⁺ in solution— especially when considering typically shorter times from solution preparation to deposition. This doesn't rule out the potential for ammonium ions to react in solutions with appreciable amounts

of base (e.g., in DMF, where dimethylamine is often a significant impurity), in solutions at elevated temperatures, during annealing, or under harsh aging conditions.

4.3.2.2 Exchange Reaction(s) in Solution

We also sought to understand the stability of the FA-adducts in solutions containing FAI to examine the extent to which substituted formamidiniums might engage in further reactions. We monitored the exchange reaction by comixing N,N'-benzylformamidinium and FAI in equimolar amounts (~0.1M) in DMSO- d_6 . We monitored the reaction by ¹H-NMR spectroscopy at times of 0, 2, 4, 6, 8, and 24 hours. The integrals were normalized using the residual DMSO peak.



Figure 4.10: ¹H-NMR spectra of mixture N,N'-benzylformamidinium and FAI at t=24h. Methine C-H peaks and benzylammonium iodide CH₂ are color coded and were used to track the reaction.

The most distinct peaks in the ¹H-NMR spectra are the methine C-H peaks which were used to monitor the exchange reaction. In figure 4.10 above, the methine peaks are shaded to match the corresponding structure on the left. A small amount of residual benzylammonium iodide from the preparation of N,N'-benzylformamidinium iodide can be observed at 4.01 ppm, corresponding to the aliphatic CH₂ protons.



Figure 4.11: Integrals of peaks from ¹H-NMR spectra of *N*,*N*'-benzylformamidinium and FAI of mixture *vs*. time. Compete spectra shown in above in Figure 4.10.

To best track the reaction progress within these complicated spectra, the integrals for each of the methine peaks (and aliphatic CH_2 protons in the case of benzylammonium) were plotted versus time. Overall, there is minimal change in the integral of each peak over time,

indicating that the bis-substituted benzylformamidinium is relatively stable, especially on the timescale of solution preparation and film deposition.

4.3.3 Synthesis and Characterization of Imidazoline and an Imidazolinium Acetate Salt

We have previously described the use of ethylene diamine as an additive for wide bandgap, tandem-relevant perovskite compositions. One of the key findings from this work was that both NMR studies on the ink chemistry and ToF-SIMs on the resultant films indicated that ethylene diamine reacted with formamidinium ion in solution to produce the 4,5dihydroimidazolium (or imidazolinium) ion (which can be considered an *N*,*N*'-disubstituted FA⁺ derivative in which the substituent bridges the N atoms). The performance improvements and stability of the devices led us to attempt to cleanly isolate the 4,5-dihydroimidazolium and use it as an additive rather than forming it in situ. We identified and explored several synthetic methods to form the neutral heterocyclic and salts of its conjugate acid.


Figure 4.12: An overview of the synthetic methods explored—the left shows methods for the preparation of neutral 4,5-dihydroimidazole whereas the right shows a method for the preparation of the acetate salt of its conjugate acid. Method C is highlighted as it was used for the scaled-up reaction.

We first tried to isolate the neutral heterocycle using method B, as the reagents required are more commonly available. This reaction may have produced some product but it was likely converted to its bicarbonate salt upon exposure to CO_2 with residual water. Subsequently we tried to isolate the acetate salt of the protonated heterocycle via method E.²⁹ While this method produced the product, there was still an appreciable amount of ethylene diammonium diacetate (~10 mol %) which was inseparable from the product (both via liquid-liquid extraction, and deprotonation and protection with *tert*-butyloxycarbonyl (BOC) protecting group followed by flash chromatography).

Methods A, C and D are all advantageous as the side product in those reactions is not water (which drastically complicates isolation of the product in B).^{23, 30-31} Methods A and C worked well "in my hands." Method C was chosen for a larger scale reaction due to the commercial availability of the acetal precursor and ease of isolation given the absence of TMS-

containing byproducts. Using this method, we prepared \sim 500 mg of neutral 4,5dihydroimidazole. The structure and purity were confirmed by ¹H-NMR in CDCl₃ and CD₃CN.

4.3.4 Characterization of Imidazoline-passivated Perovskites

While it is clear from our previous work that EDA is converted to imidazolinium and the resulting devices exhibit good performance and stability, the precise role of imidazolinium was not fully established. Studying the direct addition of imidazoline to the perovskite precursor may help to elucidate its role and may offer a more reproducible method for improving device performance and stability.



Figure 4.13: Time-resolved photoluminescence measurements of Cs17Br25 perovskite films without additive (ctrl, black trace), with 1 mol% imidazoline additive (Imn 1%, orange trace), and 5.8 mol% imidazoline additive (Imn 5.8%, purple trace) increases the lifetime.

We first sought to characterize the photoluminescence and structural properties of perovskite thin-films incorporating the imidazoline (Imn) additive. Time-resolved photoluminescence measurements shown in Figure 4.13 indicate a longer lifetime upon addition of imidazoline (Imn). Increasing the concentration of the imidazoline from 1 mol% to 5.8 mol% allows for further improvement to the PL lifetime. Structural changes to the perovskite thin films were observed with X-ray diffraction (XRD), shown below in Figure 4.14. The control film is consistent with previous reports for this composition and contains a small amount of PbI₂. Addition of 1 mol% Imn does not appreciably change the phases present, whereas upon addition of 5.8 mol% the diffraction pattern is consistent with simulations (previously reported in the literature) indicating a 1D face sharing perovskite phase (ImnHPbI)₃.³²



Figure 4.14: X-ray diffraction (XRD) patterns control (black), 1 mol% Imn (orange), and 5.8 mol% Imn (purple) pervoskite Cs17Br25 films. Asterisks indicate diffraction peaks consistent with 1D face-sharing ABX₃ formula.

We also characterized the lateral heterogeneity in the Cs17Br25 films with the Imn additive. The hyperspectral images, shown below in Figure 4.15, show that the control films are more heterogenous than the films with the Imn additive. Increasing the amount of Imn additive from 1 mol% (orange box) to 5.8 mol% increases the homogeneity of the PL and decreases the emission wavelength, an effect consistent with passivation. More homogeneous PL is associated with a lesser degree of halide segregation in mixed-cation mixed-halide perovskites.³³



Figure 4.15: Hyperspectral PL intensity map of the control (black box), 1 mol% Imn (orange box), and 5.8 mol% Imn. (purple box). Excitation was achieved with a white lamp with short pass filter at 500 nm. The emission was recorded using a 500 nm dichroic and 650 nm long pass filter.



Figure 4.16: Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements of (**A**) $C_3H_7N_2^+$ mass fragment consistent with the formation of ImnH⁺ and (**B**) $C_2H_{10}N_2^{2+}$ mass fragment consistent with the formation of EDAH₂²⁺.

Lastly, time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were carried out to verify the formation of the protonated ImnH⁺ cation. In Figure 4.16 A, it was observed that the Imn additive approach leads to a homogenous incorporation of ImnH⁺ throughout

the film, whereas the surface passivation approaches lead to a relatively sharp decreases in $C_3H_7N_2^+$ mass fragment with increased sputter time. Increasing the concentration unsurprisingly also increases the amount of Imn at the surface of the film. It is noteworthy that a surface treatment with ethylene diammonium diiodide leads to no increase at the surface over the control.

It is also useful to measure the $C_2H_{10}N_2^{2+}$ mass fragment consistent with the formation of $EDAH_2^{2+}$. In the case of the addition of Imn, there is a negligible increase in the EDA dication fragment indicating that the Imn molecule is able to be processed without degradation to EDA. Unsurprisingly treatments using EDA and EDAI₂ increase the amount of $EDAH_2^{2+}$ at the surface of the film.

4.4 Conclusion

The reactivity of several amines and ammoniums with formamidinium iodide was reported. Ammonium cations do not readily undergo transimination reactions with formamidinium iodide. This result is perhaps unsurprising when one considers the ubiquity of triple cation (CsMAFA) perovskite, where methylammonium is analogous to the amines screened here. This does not fully rule out the possibility of the reaction at elevated temperatures, or under harsh aging conditions in thin films. A neutral amine (APTMS) that has been used in PSCs was reported to undergo rapid transimination reaction, consistent with our previous observations for ethylene diamine and benzylamine additives. The transimination reaction that takes place is substantial and distinct from the previous prevailing assumption in the literature that simple proton transfer reactions are the operative and predominant reaction. Finally, a reaction product from the use of ethylene diamine in FA-containing perovskite precursors, imidazoline, was synthesized. This molecule was controllably added to perovskite precursor solutions and used as a passivation treatment, and offered similar results compared to ethylene diamine treatments (in terms of increased PL lifetime and PL homogeneity). Subsequent and ongoing work will focus on incorporating these materials into PSC devices.

4.5 References

1. Mitzi, D. B., Introduction: Perovskites. *Chem. Rev.* **2019**, *119* (5), 3033-3035.

2. Stoumpos, C. C.; Kanatzidis, M. G., The Renaissance of Halide Perovskites and Their Evolution as Emerging Semiconductors. *Acc. Chem. Res.* **2015**, *48* (10), 2791-2802.

3. Lee, M. V.; Raga, S. R.; Kato, Y.; Leyden, M. R.; Ono, L. K.; Wang, S.; Qi, Y., Transamidation of dimethylformamide during alkylammonium lead triiodide film formation for perovskite solar cells. *J. Mater. Res.* **2017**, *32* (1), 45-55.

4. Dou, B.; Wheeler, L. M.; Christians, J. A.; Moore, D. T.; Harvey, S. P.; Berry, J. J.; Barnes, F. S.; Shaheen, S. E.; van Hest, M. F. A. M., Degradation of Highly Alloyed Metal Halide Perovskite Precursor Inks: Mechanism and Storage Solutions. *ACS Energy Letters* **2018**, *3* (4), 979-985.

5. Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Grätzel, M., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy & Environmental Science* **2016**, *9* (6), 1989-1997.

6. Jariwala, S.; Kumar, R. E.; Eperon, G. E.; Shi, Y.; Fenning, D. P.; Ginger, D. S., Dimethylammonium Addition to Halide Perovskite Precursor Increases Vertical and Lateral Heterogeneity. *ACS Energy Letters* **2022**, *7* (1), 204-210.

7. Eperon, G. E.; Stone, K. H.; Mundt, L. E.; Schloemer, T. H.; Habisreutinger, S. N.; Dunfield, S. P.; Schelhas, L. T.; Berry, J. J.; Moore, D. T., The Role of Dimethylammonium in Bandgap Modulation for Stable Halide Perovskites. *ACS Energy Letters* **2020**, *5* (6), 1856-1864.

8. McMeekin, D. P.; Holzhey, P.; Fürer, S. O.; Harvey, S. P.; Schelhas, L. T.; Ball, J. M.; Mahesh, S.; Seo, S.; Hawkins, N.; Lu, J.; Johnston, M. B.; Berry, J. J.; Bach, U.; Snaith, H. J., Intermediate-phase engineering via dimethylammonium cation additive for stable perovskite solar cells. *Nature Materials* **2023**, *22* (1), 73-83.

9. Van Gompel, W. T. M.; Herckens, R.; Reekmans, G.; Ruttens, B.; D'Haen, J.; Adriaensens, P.; Lutsen, L.; Vanderzande, D., Degradation of the Formamidinium Cation and the Quantification of the Formamidinium–Methylammonium Ratio in Lead Iodide Hybrid Perovskites by Nuclear Magnetic Resonance Spectroscopy. *The Journal of Physical Chemistry C* **2018**, *122* (8), 4117-4124.

10. Kerner, R. A.; Schloemer, T. H.; Schulz, P.; Berry, J. J.; Schwartz, J.; Sellinger, A.; Rand, B. P., Amine additive reactions induced by the soft Lewis acidity of Pb2+ in halide perovskites. Part I: evidence for Pb–alkylamide formation. *Journal of Materials Chemistry C* **2019**, *7* (18), 5251-5259.

11. Kerner, R. A.; Schloemer, T. H.; Schulz, P.; Berry, J. J.; Schwartz, J.; Sellinger, A.; Rand, B. P., Amine additive reactions induced by the soft Lewis acidity of Pb2+ in halide perovskites. Part II: impacts of amido Pb impurities in methylammonium lead triiodide thin films. *Journal of Materials Chemistry C* **2019**, *7* (18), 5244-5250.

12. Hu, J.; Kerner, R. A.; Pelczer, I.; Rand, B. P.; Schwartz, J., Organoammonium-Ion-based Perovskites Can Degrade to Pb0 via Amine–Pb(II) Coordination. *ACS Energy Letters* **2021**, *6* (6), 2262-2267.

13. Xu, Y.; Xu, W.; Hu, Z.; Steele, J. A.; Wang, Y.; Zhang, R.; Zheng, G.; Li, X.; Wang, H.; Zhang, X.; Solano, E.; Roeffaers, M. B. J.; Uvdal, K.; Qing, J.; Zhang, W.; Gao, F., Impact of Amine Additives on Perovskite Precursor Aging: A Case Study of Light-Emitting Diodes. *The Journal of Physical Chemistry Letters* **2021**, *12* (25), 5836-5843.

14. Dong, Q.; Shang, W.; Yu, X.; Yin, Y.; Jiang, C.; Feng, Y.; Bian, J.; Song, B.; Jin, S.; Zhou, Y.; Wang, L.; Shi, Y., Critical Role of Organoamines in the Irreversible Degradation of a Metal Halide Perovskite Precursor Colloid: Mechanism and Inhibiting Strategy. *ACS Energy Letters* **2022**, *7* (1), 481-489.

15. Wang, X.; Fan, Y.; Wang, L.; Chen, C.; Li, Z.; Liu, R.; Meng, H.; Shao, Z.; Du, X.; Zhang, H.; Cui, G.; Pang, S., Perovskite Solution Aging: What Happened and How to Inhibit? *Chem* **2020**, *6* (6), 1369-1378.

16. Zhang, Y.; Xing, Z.; Fan, B.; Ni, Z.; Wang, F.; Hu, X.; Chen, Y., Uncovering Aging Chemistry of Perovskite Precursor Solutions and Anti-aging Mechanism of Additives. *Angew. Chem. Int. Ed.* **2023**, *62* (8), e202215799.

17. Valenzano, V.; Cesari, A.; Balzano, F.; Milella, A.; Fracassi, F.; Listorti, A.; Gigli, G.; Rizzo, A.; Uccello-Barretta, G.; Colella, S., Methylammonium-formamidinium reactivity in aged organometal halide perovskite inks. *Cell Reports Physical Science* **2021**, *2* (5), 100432.

18. Kerner, R. A.; Schutt, K.; Zhu, K.; Berry, J. J., PbI2 Reagent Impurities Catalyze Mixed-Cation Halide Perovskite Ink Degradation. *ACS Energy Letters* **2022**, *7* (12), 4333-4335.

19. Hu, J.; Xu, Z.; Murrey, T. L.; Pelczer, I.; Kahn, A.; Schwartz, J.; Rand, B. P., Triiodide Attacks the Organic Cation in Hybrid Lead Halide Perovskites: Mechanism and Suppression. *Adv. Mater.* **2023**, *35* (40), 2303373.

20. Jiang, Q.; Tong, J.; Xian, Y.; Kerner, R. A.; Dunfield, S. P.; Xiao, C.; Scheidt, R. A.; Kuciauskas, D.; Wang, X.; Hautzinger, M. P.; Tirawat, R.; Beard, M. C.; Fenning, D. P.; Berry, J. J.; Larson, B. W.; Yan, Y.; Zhu, K., Surface reaction for efficient and stable inverted perovskite solar cells. *Nature* **2022**, *611* (7935), 278-283.

21. Wang, M.; Shi, Z.; Fei, C.; Deng, Z. J. D.; Yang, G.; Dunfield, S. P.; Fenning, D. P.; Huang, J., Ammonium cations with high pKa in perovskite solar cells for improved high-temperature photostability. *Nature Energy* **2023**.

22. Spanopoulos, I.; Ke, W.; Stoumpos, C. C.; Schueller, E. C.; Kontsevoi, O. Y.; Seshadri, R.; Kanatzidis, M. G., Unraveling the Chemical Nature of the 3D "Hollow" Hybrid Halide Perovskites. *J. Am. Chem. Soc.* **2018**, *140* (17), 5728-5742.

23. Aoyagi, N.; Furusho, Y.; Sei, Y.; Endo, T., Fast equilibrium of zwitterionic adduct formation in reversible fixation–release system of CO2 by amidines under dry conditions. *Tetrahedron* **2013**, *69* (26), 5476-5480.

24. Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J., Surface passivation of perovskite film for efficient solar cells. *Nature Photonics* **2019**, *13* (7), 460-466.

25. Min, H.; Kim, M.; Lee, S.-U.; Kim, H.; Kim, G.; Choi, K.; Lee, J. H.; Seok, S. I., Efficient, stable solar cells by using inherent bandgap of α -phase formamidinium lead iodide. *Science* **2019**, *366* (6466), 749-753.

26. Perini, C. A. R.; Rojas-Gatjens, E.; Ravello, M.; Castro-Mendez, A.-F.; Hidalgo, J.; An, Y.; Kim, S.; Lai, B.; Li, R.; Silva-Acuña, C.; Correa-Baena, J.-P., Interface Reconstruction from Ruddlesden–Popper Structures Impacts Stability in Lead Halide Perovskite Solar Cells. *Adv. Mater.* **2022**, *34* (51), 2204726.

27. Shi, Y.; Rojas-Gatjens, E.; Wang, J.; Pothoof, J.; Giridharagopal, R.; Ho, K.; Jiang, F.; Taddei, M.; Yang, Z.; Sanehira, E. M.; Irwin, M. D.; Silva-Acuña, C.; Ginger, D. S., (3-Aminopropyl)trimethoxysilane Surface Passivation Improves Perovskite Solar Cell Performance by Reducing Surface Recombination Velocity. *ACS Energy Letters* **2022**, *7* (11), 4081-4088.

28. Jariwala, S.; Burke, S.; Dunfield, S.; Shallcross, R. C.; Taddei, M.; Wang, J.; Eperon, G. E.; Armstrong, N. R.; Berry, J. J.; Ginger, D. S., Reducing Surface Recombination Velocity of Methylammonium-Free Mixed-Cation Mixed-Halide Perovskites via Surface Passivation. *Chem. Mater.* **2021**, *33* (13), 5035-5044.

29. Brown, D. J.; Evans, R. F., 100. Hydropyrimidines. Part I. 1,4,5,6-Tetrahydropyrimidine and its derivatives. *Journal of the Chemical Society (Resumed)* **1962**, (0), 527-533.

30. Grundmann, C.; Kreutzberger, A., Triazines. XIII. The Ring Cleavage of s-Triazine by Primary Amines. A New Method for the Synthesis of Heterocycles1,2. *J. Am. Chem. Soc.* **1955**, 77 (24), 6559-6562.

31. Suzuki, H.; Ohashi, M.; Itoh, K.; Matsuda, I.; Ishii, Y., Reaction of Group IV Organometallic Compounds. XXXII Modified Synthesis of Imidazolidines with N,N['] - Bis(trimethylsilyl)-1,2-diamines. *Bull. Chem. Soc. Jpn.* **1975**, *48* (6), 1922-1924.

32. Taddei, M.; Smith, J. A.; Gallant, B. M.; Zhou, S.; Westbrook, R. J. E.; Shi, Y.; Wang, J.; Drysdale, J. N.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Snaith, H. J.; Ginger, D. S., Ethylenediamine Addition Improves Performance and Suppresses Phase Instabilities in Mixed-Halide Perovskites. *ACS Energy Letters* **2022**, 4265-4273.

33. Knight, A. J.; Borchert, J.; Oliver, R. D. J.; Patel, J. B.; Radaelli, P. G.; Snaith, H. J.; Johnston, M. B.; Herz, L. M., Halide Segregation in Mixed-Halide Perovskites: Influence of A-Site Cations. *ACS Energy Letters* **2021**, *6* (2), 799-808.

5 Conclusions

In chapter 1, an overview of the potential of PSCs as well as major research challenges were presented. In chapter 2, the synthesis, characterization, and material properties of two solution processable electron transport polymers were reported: a homopolymer (NDI-1) and a crosslinkable copolymer (NDI-CL) which incorporated cinnamate crosslinking groups. We demonstrated the polymer's high transparency, thermal stability, photocrosslinking, and n-doping via solution and sequential processes. Finally, we demonstrated its applicability in PSCs through characterization of solar-cell device performance relative to its uncrosslinked homopolymeric counterpart (NDI-1) in n-i-p devices with a MA-free mixed-cation mixed-halide perovskite absorber (Cs17Br15).

In chapter 3, a large photoluminescence-based screening of passivation materials was completed. Candidate passivators were screened across a variety of perovskite compositions. The photoluminescence data were somewhat inconsistent, and it was difficult to identify clear trends associated with the structures of the selected passivation molecules. A benzylammonium trifluoromethanesulfonate salt, BAOTf, was identified as a highly effective passivation molecule, allowing for the fabrication of solar cells exhibiting very low hysteresis with PCEs >19% in a MA-free mixed-cation mixed-halide perovskite absorber (Cs17Br25).

In chapter 4, the reactivity of amines and ammoniums with formamidinium salts was explored. Understanding solution reactivity of amines with formamidinium salts enabled the synthesis, isolation, and implementation of the product(s) formed in these reactions as additives and surface passivation agents in perovskites. This work helped to elucidate the role of the amine/ammonium additives in controlling FA-containing perovskite growth and crystallization processes.

5.1 Potential Innovations in Electron Transport Materials

Perhaps the most significant limitation of the side-chain NDI homopolymer and copolymer structures we studied was the relatively poor charge transport characteristics of even the n-doped polymers. In devices, we were likely able to overcome this issue because of the relatively thin layers (<5nm) of the respective polymers. As such, continued work within this area should focus on improving the electron transporting characteristics (perhaps best assessed via electron mobility measurements, especially if the polymer(s) are to be used without doping). Better electron transporting characteristics will enable thicker layers that will be required to implement these materials within inverted (p-i-n) device architectures that are most relevant for tandem-on-silicon applications.

Modifying the existing side-chain NDI polymer and copolymer structures is one clear but likely incremental step towards improving electron transport layers for PSCs. While the side chain polymer approach has worked relatively well for charge transport in various arylaminebased hole transport materials (HTMs),¹⁻² some of which exhibit hole mobilities of up to 1×10^{-4} cm² V⁻¹ s⁻¹,³⁻⁴ a survey of the literature indicates few examples of side chain electrontransporting polymers with good conductivity or electron mobility. Previous work within our group on an analogous PDI polynorbornene polymer showed a rather low electron mobility (<5 $\times 10^{-5}$ cm² V⁻¹ s⁻¹).⁵

One exception in this survey of the literature was a report of the side chain perylene diimide (PDI) polymers shown below in Figure 5.1.⁶ Both polymers showed a greater than three orders of magnitude increase in electron mobility following and annealing step at 210 °C (to a value of 1.2×10^{-3} cm² V⁻¹ s⁻¹ for both polymers). Notably, the block copolymer that was diluted with domains of insulating polystyrene showed identical mobility to the homopolymer

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following the annealing step. While higher annealing temperatures may not work for layers processed atop the perovskite, they should be compatible if processed beneath the perovskite at the transparent (front) electrode in n-i-p architectures. The lower optical transparency of PDIs in the visible region is a limitation, but it may be possible to achieve mitigate this problem by using thin films or by designing analogous polymers incorporating NDIs.



Figure 5.1: Chemical structures of the polymers: (a) poly(perylene bisimide acrylate) (PPerAcr) and (b) diblock copolymer polystyrene-*block*-poly(perylene bisimide acrylate).⁶

5.1.1 Alternative Crosslinking Approaches

While the NDI-CL copolymer was able to be crosslinked to some extent, exploring other crosslinking approaches may enable faster crosslinking times, more densely crosslinked films, and increased compatibility of the crosslinker with the electroactive NDI unit. The crosslinking times were relatively long compared to previous reports of cinnamate crosslinking. This may have been in part due to a photoinduced electron transfer from the cinnamate to the naphthalene diimide. This may also explain the lesser extent of crosslinking. As reported in chapter 2, we

have prepared a small test batch of NDI copolymer incorporating 10 mol% of a benzocyclobutene comonomer, which can dimerize at temperatures around 120 °C. Also reported in chapter 2, we have prepared a test batch of NDI copolymer incorporating 50 mol% of an NDI monomer with a cinnamate (rather than 4-methoxycinnamate), which may not be as susceptible to take part in a photoinduced electron transfer to the NDI. Finally, we only briefly explored the use of an oligomeric azide, "4Bx," in the context of sequential doping of the NDI homopolymer in chapter 2. Using azido or diazarinyl oligomers may allow for the most simple implementation of crosslinking the homopolymeric system (because of the their ability to functionalize C-H bonds in the polymer).⁷⁻⁸

5.1.2 Mainchain Electron Transporting Polymers

The limited demonstration of side-chain electron transporting polymers leads one to consider two major polymeric alternatives: conjugated polymers and non-conjugated mainchain polymers. Numerous conjugated polymers have been reported in the literature with good electron mobilities and have even been incorporated into perovskite solar cells;⁹⁻¹¹ however, the decreased transparency of these materials in the visible spectrum will increase their parasitic absorption (especially in tandem cells). This limitation led us to consider non-conjugated polymers with higher transparency, although likely at the expense of preferred morphology for charge transport in our side-chain polymers. Recently, the Baran group reported an *n*-type oligo(ethylene glycol) naphthalene diimide conjugated polymer, which was used in MAPI solar cells between a layer of PCBM and the silver cathode. Polymer films showed absorption to ~600 nm but this was likely a non-factor for the fabricated p-i-n devices which reached power conversion efficiencies greater than 17%.¹² There are likely various other *n*-type conjugated

polymers with acceptable losses in transparency as a trade-off for their superior charge transport properties.

Non-conjugated mainchain electron transporting polymers, particularly polyionenes, have been reported in the literature as effective cathode buffer layers in organic solar cells (OSCs).¹³⁻¹⁵ It may be possible to leverage these materials for perovskite solar cells. Literature reports have characterized their high transparency throughout the visible region as well as their moderate conductivities and electron mobilities. A major limitation towards the implementation of these polymers in PSCs is their limited solubility in preferred solvents for ETM deposition (especially when deposited atop the perovskite in p-i-n device configurations, where good solvents for the polymers, such as trifluoroethanol, may etch FA-containing perovskite films).¹⁶

5.1.3 Small Molecule Electron Transport Materials

Finally, non-fullerene small molecules may represent a viable alternative. As discussed in Chapter 1, using small molecules instead of polymers has several implications for the synthesis and processing of these materials. Small molecules are monodisperse, are synthesized reliably and reproducibly, and have adjustable structure-packing features.^{2, 17} Lastly, some small molecules are processable via vacuum deposition techniques, which may be advantageous for their implementation into existing semiconductor manufacturing infrastructure.¹⁸ There are several reports of PSCs incorporating NDI small molecules in efficient inverted cells.¹⁹⁻²⁰ Other non-fullerene electron transport materials such as phenazine and triazine derivatives may also be suitable.²¹⁻²²

5.2 Innovations in Passivation Studies

5.2.1 Modifications to Screening Approach

While a large number of passivation materials were screened across a series of perovskite compositions, it was difficult to draw conclusions that translated to the performance of these materials as passivators in devices. A more robust PL screening method would involve also depositing the top charge transport layer (typically C_{60} or PCBM in p-i-n devices). The contact introduces non-radiative recombination pathways that are not accounted for in the PL screening of neat thin films. This simple modification to our screening approach would enable us to more readily identify materials for reduced non-radiative losses at the inferior (at least in terms of recombination) electron selective contact in methylammonium-free wide-bandgap perovskites.²³

A variety of perovskite compositions were explored; however, narrow bandgap perovskites incorporating Sn-Pb alloys have become more prominent recently, especially for the application as bottom cells in all-perovskite tandems.²⁴⁻²⁶ Alloying the B-site cation presents new potential defects including the oxidized Sn⁴⁺ species. It is likely that the unique defects and imperfections present in this LHP compositional space will interact differently with passivators. Finally, a large data set was generated from the PL-based passivator screening. Machine learning (ML) approaches may offer a method towards understanding subtle differences in the passivation effects observed. ML approaches have recently been demonstrated to identify passivation molecules for PSCs.²⁷⁻²⁹

5.3 Elucidating Reactions of Amines and Ammoniums in Perovskites

5.3.1 Increasing the Scope

From this work and the work of others it should be apparent that the reaction of amines with formamidinium salts is almost universal. Nevertheless, the extent to which the reaction products are incorporated into films for other commonly used passivation/additive approaches is not completely clear. It would also be useful to understand the impact of thermal annealing, postdeposition effects such as thermal annealing. ToF-SIMs was used to detect the formation of formamidinium adducts in our EDA studies and could be applied to study the effects discussed above. More specifically, solution NMR experiments on films may not reflect the precise molecular structures incorporated into the film as this technique requires redissolution of the perovskite. ToF-SIMs is a relatively sensitive technique which can directly probe solid-state.

5.3.2 Single Crystal Growth of Imidazolinium-based Iodoplumbates

With the imidazoline and imidazolinium salts in hand, the next research step involves attempts to grow single crystals of their (presumably 2D) perovskites (note that the related imidazolium cation has been demonstrated to form a 2D perovskite structure).³⁰ Clean isolation of the single crystals will enable us to improve our interpretation of the XRD of Cs17Br25 films with ethylene diamine (EDA) additive.

5.4 Final Conclusions

Nobel laureate Herbert Kroemer stated the now famous phrase, "the interface is the device."³¹ This statement applies well to perovskite solar cell devices, especially in the context of this thesis, as the interfaces can introduce a variety of non-radiative recombination pathways. The design of new ETMs should not trade-off electron transporting characteristics in favor of transparency. Reiterating the conclusions discussed in section 1.2.1, photoluminescence studies on passivation materials must study the passivation material(s) in between the perovskite and the charge transport layer (to be deposited atop it in the device). Finally, work in Chapter 4 only begins to advance our understanding of and underscores the importance of investigating the complex chemistry possible in lead-halide perovskites (LHPs).

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5.5 References

1. Hüttner, S.; Sommer, M.; Steiner, U.; Thelakkat, M., Organic field effect transistors from triarylamine side-chain polymers. *Appl. Phys. Lett.* **2010**, *96* (7), 073503.

2. Tremblay, M.-H.; Schutt, K.; Zhang, Y.; Lim, J.; Lin, Y.-H.; Warby, J. H.; Barlow, S.; Snaith, H. J.; Marder, S. R., A photo-crosslinkable bis-triarylamine side-chain polymer as a hole-transport material for stable perovskite solar cells. *Sustain. Energy Fuels* **2020**, *4* (1), 190-198.

3. Pan, Z.; Peng, D.; Zhao, X.; Xu, W.; Bao, Y.; Feng, Z.; Zou, Q.; Xu, B.; Wang, Y.; Gao, H.; Yin, C.; Li, R.; Wang, J.; Huang, W., Side-Chain Functionalized Polymer Hole-Transporting Materials with Defect Passivation Effect for Highly Efficient Inverted Quasi-2D Perovskite Solar Cells. *Adv. Funct. Mater.* **2023**, *n/a* (n/a), 2304881.

4. Wu, J.; Liu, C.; Li, B.; Gu, F.; Zhang, L.; Hu, M.; Deng, X.; Qiao, Y.; Mao, Y.; Tan, W.; Tian, Y.; Xu, B., Side-Chain Polymers as Dopant-Free Hole-Transporting Materials for Perovskite Solar Cells—The Impact of Substituents' Positions in Carbazole on Device Performance. *ACS Appl. Mater. Interfaces* **2019**, *11* (30), 26928-26937.

5. Huang, C.; Potscavage, W. J.; Tiwari, S. P.; Sutcu, S.; Barlow, S.; Kippelen, B.; Marder, S. R., Polynorbornenes with pendant perylene diimides for organic electronic applications. *Polym. Chem.* **2012**, *3* (10).

6. Hüttner, S.; Sommer, M.; Thelakkat, M., n-type organic field effect transistors from perylene bisimide block copolymers and homopolymers. *Appl. Phys. Lett.* **2008**, *92* (9), 093302.

7. Lepage, M. L.; Simhadri, C.; Liu, C.; Takaffoli, M.; Bi, L.; Crawford, B.; Milani, A. S.; Wulff, J. E., A broadly applicable cross-linker for aliphatic polymers containing C–H bonds. *Science* **2019**, *366* (6467), 875-878.

8. Kim, M. J.; Lee, M.; Min, H.; Kim, S.; Yang, J.; Kweon, H.; Lee, W.; Kim, D. H.; Choi, J. H.; Ryu, D. Y.; Kang, M. S.; Kim, B.; Cho, J. H., Universal three-dimensional crosslinker for all-photopatterned electronics. *Nat. Commun.* **2020**, *11* (1), 1520.

9. Zhu, Z.; Chueh, C.-C.; Zhang, G.; Huang, F.; Yan, H.; Jen, A. K. Y., Improved Ambient-Stable Perovskite Solar Cells Enabled by a Hybrid Polymeric Electron-Transporting Layer. *ChemSusChem* **2016**, *9* (18), 2586-2591.

10. Zheng, Y.-Q.; Lei, T.; Dou, J.-H.; Xia, X.; Wang, J.-Y.; Liu, C.-J.; Pei, J., Strong Electron-Deficient Polymers Lead to High Electron Mobility in Air and Their Morphology-Dependent Transport Behaviors. *Adv. Mater.* **2016**, *28* (33), 7213-7219.

11. Yang, C.-Y.; Stoeckel, M.-A.; Ruoko, T.-P.; Wu, H.-Y.; Liu, X.; Kolhe, N. B.; Wu, Z.; Puttisong, Y.; Musumeci, C.; Massetti, M.; Sun, H.; Xu, K.; Tu, D.; Chen, W. M.; Woo, H. Y.; Fahlman, M.; Jenekhe, S. A.; Berggren, M.; Fabiano, S., A high-conductivity n-type polymeric ink for printed electronics. *Nat. Commun.* **2021**, *12* (1), 2354.

12. Sharma, A.; Singh, S.; Song, X.; Rosas Villalva, D.; Troughton, J.; Corzo, D.; Toppare, L.; Gunbas, G.; Schroeder, B. C.; Baran, D., A Nonionic Alcohol Soluble Polymer Cathode Interlayer Enables Efficient Organic and Perovskite Solar Cells. *Chem. Mater.* **2021**, *33* (22), 8602-8611.

13. Liu, Y.; Sheri, M.; Cole, M. D.; Emrick, T.; Russell, T. P., Combining Fullerenes and Zwitterions in Non-Conjugated Polymer Interlayers to Raise Solar Cell Efficiency. *Angew. Chem. Int. Ed.* **2018**, *57* (31), 9675-9678.

14. Yang, R.; Tian, J.; Liu, W.; Wang, Y.; Chen, Z.; Russell, T. P.; Liu, Y., Nonconjugated Self-Doped Polymer Zwitterions as Efficient Interlayers for High Performance Organic Solar Cells. *Chem. Mater.* **2022**, *34* (16), 7293-7301.

15. Liu, M.; Fan, P.; Hu, Q.; Russell, T. P.; Liu, Y., Naphthalene-Diimide-Based Ionenes as Universal Interlayers for Efficient Organic Solar Cells. *Angew. Chem. Int. Ed.* **2020**, *59* (41), 18131-18135.

16. Liu, J.; Deng, Y.; He, X.; Liu, G.; Li, X., 2,2,2-Trifluoroethanol-Assisted Construction of 2D/3D Perovskite Heterostructures for Efficient and Stable Perovskite Solar Cells Made in Ambient Air. *ACS Appl. Mater. Interfaces* **2023**, *15* (28), 33550-33559.

17. Lian, J.; Lu, B.; Niu, F.; Zeng, P.; Zhan, X., Electron-Transport Materials in Perovskite Solar Cells. *Small Methods* **2018**, *2* (10).

18. Momblona, C.; Gil-Escrig, L.; Bandiello, E.; Hutter, E. M.; Sessolo, M.; Lederer, K.; Blochwitz-Nimoth, J.; Bolink, H. J., Efficient vacuum deposited p-i-n and n-i-p perovskite solar cells employing doped charge transport layers. *Energy Environ. Sci.* **2016**, *9* (11), 3456-3463.

19. Jung, S. K.; Lee, D. S.; Ann, M. H.; Im, S. H.; Kim, J. H.; Kwon, O. P., Non-Fullerene Organic Electron-Transporting Materials for Perovskite Solar Cells. *ChemSusChem* **2018**, *11* (22), 3882-3892.

20. Jung, S. K.; Heo, J. H.; Lee, D. W.; Lee, S. H.; Lee, S. C.; Yoon, W.; Yun, H.; Kim, D.; Kim, J. H.; Im, S. H.; Kwon, O. P., Homochiral Asymmetric-Shaped Electron-Transporting Materials for Efficient Non-Fullerene Perovskite Solar Cells. *ChemSusChem* **2019**, *12* (1), 224-230.

21. Nakayama, K.-i.; Hashimoto, Y.; Sasabe, H.; Pu, Y.-J.; Yokoyama, M.; Kido, J., Electron Injection and Transport Properties of Phenazine Compounds with Fused Rings. *Jpn. J. Appl. Phys.* **2010**, *49* (1), 01AB11.

22. Guo, J.; Zheng, C.-J.; Ke, K.; Zhang, M.; Yang, H.-Y.; Zhao, J.-W.; He, Z.-Y.; Lin, H.; Tao, S.-L.; Zhang, X.-H., Novel triazine derivatives with deep LUMO energy levels as the electron-accepting components of exciplexes. *J. Mat. Chem. C* **2021**, *9* (3), 939-946.

23. Oliver, R. D. J.; Caprioglio, P.; Peña-Camargo, F.; Buizza, L. R. V.; Zu, F.; Ramadan, A. J.; Motti, S. G.; Mahesh, S.; McCarthy, M. M.; Warby, J. H.; Lin, Y.-H.; Koch, N.; Albrecht, S.; Herz, L. M.; Johnston, M. B.; Neher, D.; Stolterfoht, M.; Snaith, H. J., Understanding and suppressing non-radiative losses in methylammonium-free wide-bandgap perovskite solar cells. *Energy Environ. Sci.* **2022**, *15* (2), 714-726.

24. Lin, R.; Xu, J.; Wei, M.; Wang, Y.; Qin, Z.; Liu, Z.; Wu, J.; Xiao, K.; Chen, B.; Park, S. M.; Chen, G.; Atapattu, H. R.; Graham, K. R.; Xu, J.; Zhu, J.; Li, L.; Zhang, C.; Sargent, E. H.; Tan, H., All-perovskite tandem solar cells with improved grain surface passivation. *Nature* **2022**, *603* (7899), 73-78.

25. Palmstrom, A. F.; Eperon, G. E.; Leijtens, T.; Prasanna, R.; Habisreutinger, S. N.; Nemeth, W.; Gaulding, E. A.; Dunfield, S. P.; Reese, M.; Nanayakkara, S.; Moot, T.; Werner, J.; Liu, J.; To, B.; Christensen, S. T.; McGehee, M. D.; van Hest, M. F. A. M.; Luther, J. M.; Berry, J. J.; Moore, D. T., Enabling Flexible All-Perovskite Tandem Solar Cells. *Joule* 2019, *3* (9), 2193-2204.
26. Zhao, D.; Chen, C.; Wang, C.; Junda, M. M.; Song, Z.; Grice, C. R.; Yu, Y.; Li, C.; Subedi, B.; Podraza, N. J.; Zhao, X.; Fang, G.; Xiong, R.-G.; Zhu, K.; Yan, Y., Efficient two-terminal all-perovskite tandem solar cells enabled by high-quality low-bandgap absorber layers. *Nat. Energy* 2018, *3* (12), 1093-1100.

27. Huang, D.; Guo, C.; Li, Z.; Zhou, H.; Zhao, X.; Feng, Z.; Zhang, R.; Liu, M.; Liang, J.; Zhao, L.; Meng, J., Machine learning-assisted screening of effective passivation materials for P–I–N type perovskite solar cells. *J. Mat. Chem. C* **2023**, *11* (28), 9602-9610.

28. Zhi, C.; Wang, S.; Sun, S.; Li, C.; Li, Z.; Wan, Z.; Wang, H.; Li, Z.; Liu, Z., Machine-Learning-Assisted Screening of Interface Passivation Materials for Perovskite Solar Cells. *ACS Energy Lett.* **2023**, *8* (3), 1424-1433.

29. Liu, W.; Lu, Y.; Wei, D.; Huo, X.; Huang, X.; Li, Y.; Meng, J.; Zhao, S.; Qiao, B.; Liang, Z.; Xu, Z.; Song, D., Screening interface passivation materials intelligently through machine learning for highly efficient perovskite solar cells. *J. Mat. Chem. A* **2022**, *10* (34), 17782-17789.

30. Kim, J.; Hwang, T.; Lee, B.; Lee, S.; Park, K.; Park, H. H.; Park, B., An Aromatic Diamine Molecule as the A-Site Solute for Highly Durable and Efficient Perovskite Solar Cells. *Small Methods* **2019**, *3* (1), 1800361.

31. The interface is still the device. *Nat. Mater.* **2012**, *11* (2), 91-91.

Bibliography

- Lewis, N. S.; Crabtree, G.; Nozik, A. J.; Wasielewski, M. R.; Alivisatos, P.; Kung, H.; Tsao, J.; Chandler, E.; Walukiewicz, W.; Spitler, M.; Ellingson, R.; Overend, R.; Mazer, J.; Gress, M.; Horwitz, J.; Ashton, C.; Herndon, B.; Shapard, L.; Nault, R. M. Basic Research Needs for Solar Energy Utilization; April 18-21, 2005, 2005.
- 2 *International Energy Outlook 2018 (IEO2018)*; U.S. Energy Information Administration: 2018.
- Wang, M.; Shi, Z.; Fei, C.; Deng, Z. J. D.; Yang, G.; Dunfield, S. P.; Fenning, D. P.; Huang, J., Ammonium cations with high pKa in perovskite solar cells for improved high-temperature photostability. *Nat. Energy* **2023**.
- 4 Becquerel M, E., Memoire sur les Effets Electriques Produits sous l'Influence des Rayons Solaires. *Comptes Rendus Hebdomadaires des Seances de L'Academie des Sciences* 1839, 9, 561-567.
- 5 Green, M. A., The path to 25% silicon solar cell efficiency: History of silicon cell evolution. *Progress in Photovoltaics: Research and Applications* **2009**, *17* (3), 183-189.
- 6 Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T., Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. J. Am. Chem. Soc. 2009, 131 (17), 6050-6051.
- 7 National Renewable Energy Laboratory. Best Research-Cell Efficiencies, 2023. https://www.nrel.gov/pv/cell-efficiency.html (accessed 2023-07-28).
- Jena, A. K.; Kulkarni, A.; Miyasaka, T., Halide Perovskite Photovoltaics:
 Background, Status, and Future Prospects. *Chem. Rev.* 2019, *119* (5), 3036-3103.
- 9 Shockley, W.; Queisser, H. J., Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. J. Appl. Phys. 2004, 32 (3), 510-519.
- 10 Luo, D.; Su, R.; Zhang, W.; Gong, Q.; Zhu, R., Minimizing non-radiative recombination losses in perovskite solar cells. *Nature Reviews Materials* 2020, 5 (1), 44-60.
- Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J., Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* 2013, *342* (6156), 341-344.
- 12 Satpathy, R.; Pamuru, V., Chapter 4 Making of crystalline silicon solar cells. In *Solar PV Power*, Satpathy, R.; Pamuru, V., Eds. Academic Press: 2021; pp 71-134.
- 13 Miller, O. D.; Yablonovitch, E.; Kurtz, S. R., Strong Internal and External Luminescence as Solar Cells Approach the Shockley–Queisser Limit. *IEEE Journal* of Photovoltaics **2012**, *2* (3), 303-311.
- 14 Shockley, W., The Theory of p-n Junctions in Semiconductors and p-n Junction Transistors. *Bell System Technical Journal* **1949**, 28 (3), 435-489.
- 15 Caprioglio, P.; Stolterfoht, M.; Wolff, C. M.; Unold, T.; Rech, B.; Albrecht, S.; Neher, D., On the Relation between the Open-Circuit Voltage and Quasi-Fermi Level Splitting in Efficient Perovskite Solar Cells. *Adv. Energy Mater.* **2019**, *9* (33), 1901631.
- 16 Tress, W., Perovskite Solar Cells on the Way to Their Radiative Efficiency Limit -Insights Into a Success Story of High Open-Circuit Voltage and Low Recombination. *Adv. Energy Mater.* **2017**, *7* (14).

- 17 Pazos-Outón, L. M.; Szumilo, M.; Lamboll, R.; Richter, J. M.; Crespo-Quesada, M.; Abdi-Jalebi, M.; Beeson, H. J.; Vrućinić, M.; Alsari, M.; Snaith, H. J.; Ehrler, B.; Friend, R. H.; Deschler, F., Photon recycling in lead iodide perovskite solar cells. *Science* 2016, 351 (6280), 1430-1433.
- 18 Sproul, A. B., Dimensionless solution of the equation describing the effect of surface recombination on carrier decay in semiconductors. *J. Appl. Phys.* **1994,** *76* (5), 2851-2854.
- 19 Weiss, T. P.; Bissig, B.; Feurer, T.; Carron, R.; Buecheler, S.; Tiwari, A. N., Bulk and surface recombination properties in thin film semiconductors with different surface treatments from time-resolved photoluminescence measurements. *Scientific Reports* **2019**, *9* (1), 5385.
- 20 Green, M. A.; Ho-Baillie, A.; Snaith, H. J., The emergence of perovskite solar cells. *Nature Photonics* **2014**, *8* (7), 506-514.
- 21 Pazoki, M.; Edvinsson, T., Metal replacement in perovskite solar cell materials: chemical bonding effects and optoelectronic properties. *Sustainable Energy Fuels* **2018,** *2* (7), 1430-1445.
- 22 Goldschmidt, V. M., Die Gesetze der Krystallochemie. *Naturwissenschaften* **1926**, *14* (21), 477-485.
- 23 Kieslich, G.; Sun, S.; Cheetham, A. K., Solid-state principles applied to organic– inorganic perovskites: new tricks for an old dog. *Chemical Science* **2014**, *5* (12), 4712-4715.
- Liu, D.; Zha, W.; Guo, Y.; Sa, R., Insight into the Improved Phase Stability of CsPbI3 from First-Principles Calculations. *ACS Omega* **2020**, *5* (1), 893-896.
- Quarti, C.; Mosconi, E.; Ball, J. M.; D'Innocenzo, V.; Tao, C.; Pathak, S.; Snaith, H. J.; Petrozza, A.; De Angelis, F., Structural and optical properties of methylammonium lead iodide across the tetragonal to cubic phase transition: implications for perovskite solar cells. *Energy & Environmental Science* 2016, 9 (1), 155-163.
- 26 Bonadio, A.; Sabino, F. P.; Freitas, A. L. M.; Felez, M. R.; Dalpian, G. M.; Souza, J. A., Comparing the Cubic and Tetragonal Phases of MAPbI3 at Room Temperature. *Inorg. Chem.* 2023, 62 (19), 7533-7544.
- 27 Ma, F.; Li, J.; Li, W.; Lin, N.; Wang, L.; Qiao, J., Stable α/δ phase junction of formamidinium lead iodide perovskites for enhanced near-infrared emission. *Chemical Science* 2017, 8 (1), 800-805.
- 28 Montecucco, R.; Quadrivi, E.; Po, R.; Grancini, G., All-Inorganic Cesium-Based Hybrid Perovskites for Efficient and Stable Solar Cells and Modules. *Adv. Energy Mater.* **2021**, *11* (23), 2100672.
- 29 Tremblay, M.-H.; Boyington, A.; Rigin, S.; Jiang, J.; Bacsa, J.; Al Kurdi, K.; Khrustalev, V. N.; Pachter, R.; Timofeeva, T. V.; Jui, N.; Barlow, S.; Marder, S. R., Hybrid Organic Lead Iodides: Role of Organic Cation Structure in Obtaining 1D Chains of Face-Sharing Octahedra vs 2D Perovskites. *Chem. Mater.* 2022, 34 (3), 935-946.
- 30 Metcalf, I.; Sidhik, S.; Zhang, H.; Agrawal, A.; Persaud, J.; Hou, J.; Even, J.; Mohite, A. D., Synergy of 3D and 2D Perovskites for Durable, Efficient Solar Cells and Beyond. *Chem. Rev.* **2023**, *123* (15), 9565-9652.

- Proppe, A. H.; Johnston, A.; Teale, S.; Mahata, A.; Quintero-Bermudez, R.; Jung, E. H.; Grater, L.; Cui, T.; Filleter, T.; Kim, C.-Y.; Kelley, S. O.; De Angelis, F.; Sargent, E. H., Multication perovskite 2D/3D interfaces form via progressive dimensional reduction. *Nature Communications* 2021, *12* (1), 3472.
- 32 Mao, L.; Stoumpos, C. C.; Kanatzidis, M. G., Two-Dimensional Hybrid Halide Perovskites: Principles and Promises. J. Am. Chem. Soc. **2019**, 141 (3), 1171-1190.
- 33 Sarritzu, V.; Sestu, N.; Marongiu, D.; Chang, X.; Wang, Q.; Masi, S.; Colella, S.; Rizzo, A.; Gocalinska, A.; Pelucchi, E.; Mercuri, M. L.; Quochi, F.; Saba, M.; Mura, A.; Bongiovanni, G., Direct or Indirect Bandgap in Hybrid Lead Halide Perovskites? Advanced Optical Materials 2018, 6 (10), 1701254.
- Miyata, A.; Mitioglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J., Direct measurement of the exciton binding energy and effective masses for charge carriers in organic–inorganic tri-halide perovskites. *Nature Physics* 2015, *11* (7), 582-587.
- 35 Herz, L. M., Charge-Carrier Mobilities in Metal Halide Perovskites: Fundamental Mechanisms and Limits. *ACS Energy Letters* **2017**, *2* (7), 1539-1548.
- 36 Stoumpos, C. C.; Kanatzidis, M. G., The Renaissance of Halide Perovskites and Their Evolution as Emerging Semiconductors. *Acc. Chem. Res.* **2015**, *48* (10), 2791-2802.
- 37 Elumalai, N. K.; Mahmud, M. A.; Wang, D.; Uddin, A. Perovskite Solar Cells: Progress and Advancements *Energies* [Online], 2016.
- 38 Umebayashi, T.; Asai, K.; Kondo, T.; Nakao, A., Electronic structures of lead iodide based low-dimensional crystals. *Physical Review B* **2003**, *67* (15), 155405.
- 39 Xiao, Z.; Zhou, Y.; Hosono, H.; Kamiya, T.; Padture, N. P., Bandgap Optimization of Perovskite Semiconductors for Photovoltaic Applications. *Chemistry – A European Journal* 2018, 24 (10), 2305-2316.
- 40 Tao, S.; Schmidt, I.; Brocks, G.; Jiang, J.; Tranca, I.; Meerholz, K.; Olthof, S., Absolute energy level positions in tin- and lead-based halide perovskites. *Nature Communications* **2019**, *10* (1), 2560.
- 41 Manser, J. S.; Christians, J. A.; Kamat, P. V., Intriguing Optoelectronic Properties of Metal Halide Perovskites. *Chem. Rev.* **2016**, *116* (21), 12956-13008.
- 42 Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J., Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science* **2012**, *338* (6107), 643-647.
- 43 Park, N.-G., Perovskite solar cells: an emerging photovoltaic technology. *Mater. Today* **2015**, *18* (2), 65-72.
- Liu, M.; Johnston, M. B.; Snaith, H. J., Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* **2013**, *501* (7467), 395-398.
- 45 Roldán-Carmona, C.; Malinkiewicz, O.; Betancur, R.; Longo, G.; Momblona, C.; Jaramillo, F.; Camacho, L.; Bolink, H. J., High efficiency single-junction semitransparent perovskite solar cells. *Energy & Environmental Science* 2014, 7 (9), 2968-2973.
- 46 Seo, J.; Park, S.; Chan Kim, Y.; Jeon, N. J.; Noh, J. H.; Yoon, S. C.; Seok, S. I., Benefits of very thin PCBM and LiF layers for solution-processed p–i–n perovskite solar cells. *Energy & Environmental Science* **2014**, *7* (8), 2642-2646.

- 47 Nie, W.; Tsai, H.; Asadpour, R.; Blancon, J.-C.; Neukirch, A. J.; Gupta, G.; Crochet, J. J.; Chhowalla, M.; Tretiak, S.; Alam, M. A.; Wang, H.-L.; Mohite, A. D., High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science* 2015, *347* (6221), 522-525.
- 48 Lin, X.; Cui, D.; Luo, X.; Zhang, C.; Han, Q.; Wang, Y.; Han, L., Efficiency progress of inverted perovskite solar cells. *Energy & Environmental Science* **2020**, *13* (11), 3823-3847.
- Yoo, J. J.; Seo, G.; Chua, M. R.; Park, T. G.; Lu, Y.; Rotermund, F.; Kim, Y.-K.; Moon, C. S.; Jeon, N. J.; Correa-Baena, J.-P.; Bulović, V.; Shin, S. S.; Bawendi, M. G.; Seo, J., Efficient perovskite solar cells via improved carrier management. *Nature* 2021, *590* (7847), 587-593.
- 50 Yuan, Q.; Lohmann, K. B.; Oliver, R. D. J.; Ramadan, A. J.; Yan, S.; Ball, J. M.; Christoforo, M. G.; Noel, N. K.; Snaith, H. J.; Herz, L. M.; Johnston, M. B., Thermally Stable Perovskite Solar Cells by All-Vacuum Deposition. ACS Applied Materials & Interfaces 2023, 15 (1), 772-781.
- 51 Momblona, C.; Gil-Escrig, L.; Bandiello, E.; Hutter, E. M.; Sessolo, M.; Lederer, K.; Blochwitz-Nimoth, J.; Bolink, H. J., Efficient vacuum deposited p-i-n and n-i-p perovskite solar cells employing doped charge transport layers. *Energy Environ. Sci.* 2016, 9 (11), 3456-3463.
- 52 Shikoh, A. S.; Polyakov, A., A Quantitative Analysis of the Research Trends in Perovskite Solar Cells in 2009–2019. *physica status solidi (a)* **2020**, *217* (23), 2000441.
- 53 Chen, B.; Rudd, P. N.; Yang, S.; Yuan, Y.; Huang, J., Imperfections and their passivation in halide perovskite solar cells. *Chem. Soc. Rev.* **2019**, *48* (14), 3842-3867.
- 54 Yin, W.-J.; Shi, T.; Yan, Y., Unusual defect physics in CH3NH3PbI3 perovskite solar cell absorber. *Appl. Phys. Lett.* **2014**, *104* (6), 063903.
- 55 Yang, S.; Dai, J.; Yu, Z.; Shao, Y.; Zhou, Y.; Xiao, X.; Zeng, X. C.; Huang, J., Tailoring Passivation Molecular Structures for Extremely Small Open-Circuit Voltage Loss in Perovskite Solar Cells. J. Am. Chem. Soc. 2019, 141 (14), 5781-5787.
- 56 Noel, N. K.; Abate, A.; Stranks, S. D.; Parrott, E. S.; Burlakov, V. M.; Goriely, A.; Snaith, H. J., Enhanced Photoluminescence and Solar Cell Performance via Lewis Base Passivation of Organic–Inorganic Lead Halide Perovskites. ACS Nano 2014, 8 (10), 9815-9821.
- 57 Wang, F.; Geng, W.; Zhou, Y.; Fang, H.-H.; Tong, C.-J.; Loi, M. A.; Liu, L.-M.; Zhao, N., Phenylalkylamine Passivation of Organolead Halide Perovskites Enabling High-Efficiency and Air-Stable Photovoltaic Cells. *Adv. Mater.* **2016**, *28* (45), 9986-9992.
- 58 Palazon, F.; Pérez-del-Rey, D.; Marras, S.; Prato, M.; Sessolo, M.; Bolink, H. J.; Manna, L., Coating Evaporated MAPI Thin Films with Organic Molecules: Improved Stability at High Temperature and Implementation in High-Efficiency Solar Cells. ACS Energy Letters 2018, 3 (4), 835-839.
- 59 Taddei, M.; Smith, J. A.; Gallant, B. M.; Zhou, S.; Westbrook, R. J. E.; Shi, Y.; Wang, J.; Drysdale, J. N.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Snaith, H. J.; Ginger, D. S., Ethylenediamine Addition Improves Performance and Suppresses

Phase Instabilities in Mixed-Halide Perovskites. *ACS Energy Letters* **2022**, 4265-4273.

- Jiang, Q.; Tong, J.; Xian, Y.; Kerner, R. A.; Dunfield, S. P.; Xiao, C.; Scheidt, R. A.; Kuciauskas, D.; Wang, X.; Hautzinger, M. P.; Tirawat, R.; Beard, M. C.; Fenning, D. P.; Berry, J. J.; Larson, B. W.; Yan, Y.; Zhu, K., Surface reaction for efficient and stable inverted perovskite solar cells. *Nature* 2022, *611* (7935), 278-283.
- Abate, A.; Saliba, M.; Hollman, D. J.; Stranks, S. D.; Wojciechowski, K.; Avolio, R.; Grancini, G.; Petrozza, A.; Snaith, H. J., Supramolecular Halogen Bond Passivation of Organic–Inorganic Halide Perovskite Solar Cells. *Nano Lett.* 2014, *14* (6), 3247-3254.
- 62 Shao, Y.; Xiao, Z.; Bi, C.; Yuan, Y.; Huang, J., Origin and elimination of photocurrent hysteresis by fullerene passivation in CH3NH3PbI3 planar heterojunction solar cells. *Nature Communications* **2014**, *5* (1), 5784.
- 63 Abdi-Jalebi, M.; Andaji-Garmaroudi, Z.; Cacovich, S.; Stavrakas, C.; Philippe, B.; Richter, J. M.; Alsari, M.; Booker, E. P.; Hutter, E. M.; Pearson, A. J.; Lilliu, S.; Savenije, T. J.; Rensmo, H.; Divitini, G.; Ducati, C.; Friend, R. H.; Stranks, S. D., Maximizing and stabilizing luminescence from halide perovskites with potassium passivation. *Nature* **2018**, *555* (7697), 497-501.
- Zhang, M.; Yun, J. S.; Ma, Q.; Zheng, J.; Lau, C. F. J.; Deng, X.; Kim, J.; Kim, D.;
 Seidel, J.; Green, M. A.; Huang, S.; Ho-Baillie, A. W. Y., High-Efficiency
 Rubidium-Incorporated Perovskite Solar Cells by Gas Quenching. ACS Energy
 Letters 2017, 2 (2), 438-444.
- 65 Jokar, E.; Chien, C.-H.; Fathi, A.; Rameez, M.; Chang, Y.-H.; Diau, E. W.-G., Slow surface passivation and crystal relaxation with additives to improve device performance and durability for tin-based perovskite solar cells. *Energy & Environmental Science* **2018**, *11* (9), 2353-2362.
- 66 Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J., Surface passivation of perovskite film for efficient solar cells. *Nature Photonics* 2019, *13* (7), 460-466.
- 67 Wang, Z.; Lin, Q.; Chmiel, F. P.; Sakai, N.; Herz, L. M.; Snaith, H. J., Efficient ambient-air-stable solar cells with 2D–3D heterostructured butylammoniumcaesium-formamidinium lead halide perovskites. *Nature Energy* **2017**, *2* (9), 17135.
- 68 Hu, Y.; Schlipf, J.; Wussler, M.; Petrus, M. L.; Jaegermann, W.; Bein, T.; Müller-Buschbaum, P.; Docampo, P., Hybrid Perovskite/Perovskite Heterojunction Solar Cells. ACS Nano 2016, 10 (6), 5999-6007.
- 69 Shi, Y.; Rojas-Gatjens, E.; Wang, J.; Pothoof, J.; Giridharagopal, R.; Ho, K.; Jiang, F.; Taddei, M.; Yang, Z.; Sanehira, E. M.; Irwin, M. D.; Silva-Acuña, C.; Ginger, D. S., (3-Aminopropyl)trimethoxysilane Surface Passivation Improves Perovskite Solar Cell Performance by Reducing Surface Recombination Velocity. ACS Energy Letters 2022, 7 (11), 4081-4088.
- deQuilettes, D. W.; Koch, S.; Burke, S.; Paranji, R. K.; Shropshire, A. J.; Ziffer, M. E.; Ginger, D. S., Photoluminescence Lifetimes Exceeding 8 µs and Quantum Yields Exceeding 30% in Hybrid Perovskite Thin Films by Ligand Passivation. ACS Energy Letters 2016, 1 (2), 438-444.
- 71 Jariwala, S.; Burke, S.; Dunfield, S.; Shallcross, R. C.; Taddei, M.; Wang, J.; Eperon, G. E.; Armstrong, N. R.; Berry, J. J.; Ginger, D. S., Reducing Surface

Recombination Velocity of Methylammonium-Free Mixed-Cation Mixed-Halide Perovskites via Surface Passivation. *Chem. Mater.* **2021**, *33* (13), 5035-5044.

- 72 Said, A. A.; Xie, J.; Zhang, Q., Recent Progress in Organic Electron Transport Materials in Inverted Perovskite Solar Cells. *Small* **2019**, *15* (27), e1900854.
- 73 Lian, J.; Lu, B.; Niu, F.; Zeng, P.; Zhan, X., Electron-Transport Materials in Perovskite Solar Cells. *Small Methods* **2018**, *2* (10).
- 74 Wang, J.; Fu, W.; Jariwala, S.; Sinha, I.; Jen, A. K. Y.; Ginger, D. S., Reducing Surface Recombination Velocities at the Electrical Contacts Will Improve Perovskite Photovoltaics. ACS Energy Letters 2019, 4 (1), 222-227.
- 75 Tremblay, M.-H.; Schutt, K.; Zhang, Y.; Lim, J.; Lin, Y.-H.; Warby, J. H.; Barlow, S.; Snaith, H. J.; Marder, S. R., A photo-crosslinkable bis-triarylamine side-chain polymer as a hole-transport material for stable perovskite solar cells. *Sustainable Energy Fuels* 2020, *4* (1), 190-198.
- 76 Wang, J.; Liu, Y.; Chen, X.; Chen, C.; Chen, P.; Wang, Z.; Duan, Y., Functional Metal Oxides in Perovskite Solar Cells. *ChemPhysChem* **2019**, *20* (20), 2580-2586.
- Al-Ashouri, A.; Magomedov, A.; Roß, M.; Jošt, M.; Talaikis, M.; Chistiakova, G.; Bertram, T.; Márquez, J. A.; Köhnen, E.; Kasparavičius, E.; Levcenco, S.; Gil-Escrig, L.; Hages, C. J.; Schlatmann, R.; Rech, B.; Malinauskas, T.; Unold, T.; Kaufmann, C. A.; Korte, L.; Niaura, G.; Getautis, V.; Albrecht, S., Conformal monolayer contacts with lossless interfaces for perovskite single junction and monolithic tandem solar cells. *Energy & Environmental Science* 2019, *12* (11), 3356-3369.
- 78 Cao, Z.; Li, C.; Deng, X.; Wang, S.; Yuan, Y.; Chen, Y.; Wang, Z.; Liu, Y.; Ding, L.; Hao, F., Metal oxide alternatives for efficient electron transport in perovskite solar cells: beyond TiO2 and SnO2. *Journal of Materials Chemistry A* 2020, *8* (38), 19768-19787.
- Smith, J. A.; Game, O. S.; Bishop, J. E.; Spooner, E. L. K.; Kilbride, R. C.;
 Greenland, C.; Jayaprakash, R.; Alanazi, T. I.; Cassella, E. J.; Tejada, A.;
 Chistiakova, G.; Wong-Stringer, M.; Routledge, T. J.; Parnell, A. J.; Hammond, D.
 B.; Lidzey, D. G., Rapid Scalable Processing of Tin Oxide Transport Layers for
 Perovskite Solar Cells. ACS Applied Energy Materials 2020, 3 (6), 5552-5562.
- 80 Ranjan, S.; Ranjan, R.; Tyagi, A.; Rana, K. S.; Soni, A.; Kodali, H. K.; Dalal, V.; Singh, A.; Garg, A.; Nalwa, K. S.; Gupta, R. K., Low-Temperature Microwave Processed TiO2 as an Electron Transport Layer for Enhanced Performance and Atmospheric Stability in Planar Perovskite Solar Cells. ACS Applied Energy Materials 2022, 5 (3), 2679-2696.
- 81 Wang, J. T.-W.; Ball, J. M.; Barea, E. M.; Abate, A.; Alexander-Webber, J. A.; Huang, J.; Saliba, M.; Mora-Sero, I.; Bisquert, J.; Snaith, H. J.; Nicholas, R. J., Low-Temperature Processed Electron Collection Layers of Graphene/TiO2 Nanocomposites in Thin Film Perovskite Solar Cells. *Nano Lett.* 2014, *14* (2), 724-730.
- 82 Ke, W.; Zhao, D.; Cimaroli, A. J.; Grice, C. R.; Qin, P.; Liu, Q.; Xiong, L.; Yan, Y.; Fang, G., Effects of annealing temperature of tin oxide electron selective layers on the performance of perovskite solar cells. *Journal of Materials Chemistry A* 2015, 3 (47), 24163-24168.

- 83 Wu, P.; Wang, S.; Li, X.; Zhang, F., Advances in SnO2-based perovskite solar cells: from preparation to photovoltaic applications. *Journal of Materials Chemistry A* 2021, 9 (35), 19554-19588.
- 84 Luo, J.; Wang, Y.; Zhang, Q., Progress in perovskite solar cells based on ZnO nanostructures. *Solar Energy* **2018**, *163*, 289-306.
- 85 Liu, J.; Gao, C.; Luo, L.; Ye, Q.; He, X.; Ouyang, L.; Guo, X.; Zhuang, D.; Liao, C.; Mei, J.; Lau, W., Low-temperature, solution processed metal sulfide as an electron transport layer for efficient planar perovskite solar cells. *Journal of Materials Chemistry A* 2015, *3* (22), 11750-11755.
- 86 Zhu, L.; Shao, Z.; Ye, J.; Zhang, X.; Pan, X.; Dai, S., Mesoporous BaSnO3 layer based perovskite solar cells. *Chem. Commun.* **2016**, *52* (5), 970-973.
- 87 Ling, X.; Yuan, J.; Liu, D.; Wang, Y.; Zhang, Y.; Chen, S.; Wu, H.; Jin, F.; Wu, F.; Shi, G.; Tang, X.; Zheng, J.; Liu, S.; Liu, Z.; Ma, W., Room-Temperature Processed Nb2O5 as the Electron-Transporting Layer for Efficient Planar Perovskite Solar Cells. ACS Applied Materials & Interfaces 2017, 9 (27), 23181-23188.
- 88 Neophytou, M.; De Bastiani, M.; Gasparini, N.; Aydin, E.; Ugur, E.; Seitkhan, A.; Moruzzi, F.; Choaie, Y.; Ramadan, A. J.; Troughton, J. R.; Hallani, R.; Savva, A.; Tsetseris, L.; Inal, S.; Baran, D.; Laquai, F.; Anthopoulos, T. D.; Snaith, H. J.; De Wolf, S.; McCulloch, I., Enhancing the Charge Extraction and Stability of Perovskite Solar Cells Using Strontium Titanate (SrTiO3) Electron Transport Layer. ACS Applied Energy Materials 2019, 2 (11), 8090-8097.
- 89 Lin, L.; Jones, T. W.; Yang, T. C.-J.; Duffy, N. W.; Li, J.; Zhao, L.; Chi, B.; Wang, X.; Wilson, G. J., Inorganic Electron Transport Materials in Perovskite Solar Cells. *Adv. Funct. Mater.* 2021, *31* (5), 2008300.
- 90 Jung, S. K.; Lee, D. S.; Ann, M. H.; Im, S. H.; Kim, J. H.; Kwon, O. P., Non-Fullerene Organic Electron-Transporting Materials for Perovskite Solar Cells. *ChemSusChem* 2018, 11 (22), 3882-3892.
- 91 Stolterfoht, M.; Wolff, C. M.; Márquez, J. A.; Zhang, S.; Hages, C. J.; Rothhardt, D.; Albrecht, S.; Burn, P. L.; Meredith, P.; Unold, T.; Neher, D., Visualization and suppression of interfacial recombination for high-efficiency large-area pin perovskite solar cells. *Nature Energy* **2018**, *3* (10), 847-854.
- Warby, J.; Zu, F.; Zeiske, S.; Gutierrez-Partida, E.; Frohloff, L.; Kahmann, S.;
 Frohna, K.; Mosconi, E.; Radicchi, E.; Lang, F.; Shah, S.; Peña-Camargo, F.;
 Hempel, H.; Unold, T.; Koch, N.; Armin, A.; De Angelis, F.; Stranks, S. D.; Neher,
 D.; Stolterfoht, M., Understanding Performance Limiting Interfacial Recombination
 in pin Perovskite Solar Cells. *Adv. Energy Mater.* 2022, *12* (12), 2103567.
- 93 Quinn, J. T. E.; Zhu, J.; Li, X.; Wang, J.; Li, Y., Recent progress in the development of n-type organic semiconductors for organic field effect transistors. *Journal of Materials Chemistry C* **2017**, *5* (34), 8654-8681.
- 94 Jiang, K.; Wu, F.; Zhu, L.; Yan, H., Naphthodiperylenetetraimide-Based Polymer as Electron-Transporting Material for Efficient Inverted Perovskite Solar Cells. ACS Applied Materials & Interfaces 2018, 10 (42), 36549-36555.
- 95 Jung, S. K.; Heo, J. H.; Lee, D. W.; Lee, S. H.; Lee, S. C.; Yoon, W.; Yun, H.; Kim, D.; Kim, J. H.; Im, S. H.; Kwon, O. P., Homochiral Asymmetric-Shaped Electron-Transporting Materials for Efficient Non-Fullerene Perovskite Solar Cells. *ChemSusChem* 2019, 12 (1), 224-230.

- 96 Jung, S.-K.; Heo, J. H.; Lee, D. W.; Lee, S.-C.; Lee, S.-H.; Yoon, W.; Yun, H.; Im, S. H.; Kim, J. H.; Kwon, O. P., Nonfullerene Electron Transporting Material Based on Naphthalene Diimide Small Molecule for Highly Stable Perovskite Solar Cells with Efficiency Exceeding 20%. *Adv. Funct. Mater.* 2018, 28 (20).
- 97 Zhu, Z.; Chueh, C.-C.; Zhang, G.; Huang, F.; Yan, H.; Jen, A. K. Y., Improved Ambient-Stable Perovskite Solar Cells Enabled by a Hybrid Polymeric Electron-Transporting Layer. *ChemSusChem* **2016**, *9* (18), 2586-2591.
- Wang, N.; Zhao, K.; Ding, T.; Liu, W.; Ahmed, A. S.; Wang, Z.; Tian, M.; Sun, X. W.; Zhang, Q., Improving Interfacial Charge Recombination in Planar Heterojunction Perovskite Photovoltaics with Small Molecule as Electron Transport Layer. *Adv. Energy Mater.* 2017, 7 (18).
- 99 Wojciechowski, K.; Ramirez, I.; Gorisse, T.; Dautel, O.; Dasari, R.; Sakai, N.; Hardigree, J. M.; Song, S.; Marder, S.; Riede, M.; Wantz, G.; Snaith, H. J., Cross-Linkable Fullerene Derivatives for Solution-Processed n–i–p Perovskite Solar Cells. ACS Energy Letters 2016, 1 (4), 648-653.
- 100 Bai, Y.; Dong, Q.; Shao, Y.; Deng, Y.; Wang, Q.; Shen, L.; Wang, D.; Wei, W.; Huang, J., Enhancing stability and efficiency of perovskite solar cells with crosslinkable silane-functionalized and doped fullerene. *Nature Communications* 2016, 7 (1), 12806.
- 101 Zhu, Z.; Zhao, D.; Chueh, C.-C.; Shi, X.; Li, Z.; Jen, A. K. Y., Highly Efficient and Stable Perovskite Solar Cells Enabled by All-Crosslinked Charge-Transporting Layers. *Joule* **2018**, *2* (1), 168-183.
- 102 Zheng, L.; Mukherjee, S.; Wang, K.; Hay, M. E.; Boudouris, B. W.; Gong, X., Radical polymers as interfacial layers in inverted hybrid perovskite solar cells. *Journal of Materials Chemistry A* **2017**, *5* (45), 23831-23839.
- 103 Xu, J.; Voznyy, O.; Comin, R.; Gong, X.; Walters, G.; Liu, M.; Kanjanaboos, P.; Lan, X.; Sargent, E. H., Crosslinked Remote-Doped Hole-Extracting Contacts Enhance Stability under Accelerated Lifetime Testing in Perovskite Solar Cells. *Adv. Mater.* 2016, 28 (14), 2807-15.
- 104 National Renewable Energy Laboratory. Best Research-Cell Efficiencies , 2023. https://www.nrel.gov/pv/cell-efficiency.html (accessed 2023-07-28).
- 105 Lian, J.; Lu, B.; Niu, F.; Zeng, P.; Zhan, X. Electron-Transport Materials in Perovskite Solar Cells. *Small Methods* **2018**, *2* (10), 1–27.
- Lin, L.; Jones, T. W.; Yang, T. C. J.; Duffy, N. W.; Li, J.; Zhao, L.; Chi, B.; Wang, X.; Wilson, G. J. Inorganic Electron Transport Materials in Perovskite Solar Cells. *Adv. Funct. Mater.* 2021, *31* (5), 2008300.
- 107 Leijtens, T.; Eperon, G. E.; Pathak, S.; Abate, A.; Lee, M. M.; Snaith, H. J. Overcoming Ultraviolet Light Instability of Sensitized TiO₂ with Meso-Superstructured Organometal Tri-Halide Perovskite Solar Cells. *Nat. Commun.* 2013, 4, 1–8.
- 108 Ranjan, S.; Ranjan, R.; Tyagi, A.; Rana, K. S.; Soni, A.; Kodali, H. K.; Dalal, V.; Singh, A.; Garg, A.; Nalwa, K. S.; Gupta, R. K. Low-Temperature Microwave Processed TiO₂ as an Electron Transport Layer for Enhanced Performance and Atmospheric Stability in Planar Perovskite Solar Cells. ACS Appl. Energy Mater. 2022, 5 (3), 2679–2696.

- 109 Zhou, H.; Chen, Q.; Li, G.; Luo, S.; Song, T. B.; Duan, H. S.; Hong, Z. R.; You, J. B.; Liu, Y.S.; Yang, Y. Interface Engineering of Highly Efficient Perovskite Solar Cells. *Science.* 2014, 345 (6196), 542–546.
- 110 Hu, W.; Yang, S.; Yang, S. Surface Modification of TiO₂ for Perovskite Solar Cells. *Trends Chem.* 2020, 2 (2), 148–162.
- Smith, J. A.; Game, O. S.; Bishop, J. E.; Spooner, E. L. K.; Kilbride, R. C.; Greenland, C.; Jayaprakash, R.; Alanazi, T. I.; Alanazi, T. I.; Cassella, E. J.; Tejada, A.; Tejada, A.; Chistiakova, G.; Wong-Stringer, M.; Routledge, T. J.; Parnell, A. J.; Hammond, D. B.; Lidzey, D. G. Rapid Scalable Processing of Tin Oxide Transport Layers for Perovskite Solar Cells. ACS Appl. Energy Mater. 2020, 3 (6), 5552–5562.
- 112 Anaraki, E. H.; Kermanpur, A.; Steier, L.; Domanski, K.; Matsui, T.; Tress, W.; Saliba, M.; Abate, A.; Grätzel, M.; Hagfeldt, A.; Correa-Baena, J. P. Highly Efficient and Stable Planar Perovskite Solar Cells by Solution-Processed Tin Oxide. *Energy Environ. Sci.* **2016**, *9* (10), 3128–3134.
- 113 Luo, J.; Wang, Y.; Zhang, Q. Progress in Perovskite Solar Cells Based on ZnO Nanostructures. *Sol. Energy* **2018**, *163*, 289–306.
- Liu, J.; Gao, C.; Luo, L.; Ye, Q.; He, X.; Ouyang, L.; Guo, X.; Zhuang, D.; Liao, C.; Mei, J.; Lau, W. Low-Temperature, Solution Processed Metal Sulfide as an Electron Transport Layer for Efficient Planar Perovskite Solar Cells. *J. Mater. Chem. A* 2015, 3 (22), 11750–11755.
- 115 Zhu, L.; Shao, Z.; Ye, J.; Zhang, X.; Pan, X.; Dai, S. Mesoporous BaSnO₃ Layer Based Perovskite Solar Cells. *Chem. Commun.* **2016**, *52* (5), 970–973.
- 116 Ling, X.; Yuan, J.; Liu, D.; Wang, Y.; Zhang, Y.; Chen, S.; Wu, H.; Jin, F.; Wu, F.; Shi, G.; Tang, X.; Zheng, J.; Liu, S.; Liu, Z.; Ma, W. Room-Temperature Processed Nb₂O₅ as the Electron-Transporting Layer for Efficient Planar Perovskite Solar Cells. ACS Appl. Mater. Interfaces 2017, 9 (27), 23181–23188.
- 117 Neophytou, M.; De Bastiani, M.; Gasparini, N.; Aydin, E.; Ugur, E.; Seitkhan, A.; Moruzzi, F.; Choaie, Y.; Ramadan, A. J.; Troughton, J. R.; Hallani, R.; Savva, A.; Tsetseris, L.; Inal, S.; Baran, D.; Laquai, F.; Anthopoulos, T. D.; Snaith, H. J.; De Wolf, S.; McCulloch, I. Enhancing the Charge Extraction and Stability of Perovskite Solar Cells Using Strontium Titanate (SrTiO₃) Electron Transport Layer. *ACS Appl. Energy Mater.* **2019**, 2(11), 8090-8097.
- 118 Jameel, M. A.; Yang, T. C. J.; Wilson, G. J.; Evans, R. A.; Gupta, A.; Langford, S. J. Naphthalene Diimide-Based Electron Transport Materials for Perovskite Solar Cells. *J. Mater. Chem. A* 2021, 9 (48), 27170–27192.
- 119 Wang, J.; Fu, W.; Jariwala, S.; Sinha, I.; Jen, A. K. Y.; Ginger, D. S. Reducing Surface Recombination Velocities at the Electrical Contacts Will Improve Perovskite Photovoltaics. *ACS Energy Lett.* **2019**, *4* (1), 222–227.
- Yoon, H.; Kang, S. M.; Lee, J. K.; Choi, M. Hysteresis-Free Low-Temperature-Processed Planar Perovskite Solar Cells with 19.1% Efficiency. *Energy Environ. Sci.* 2016, 9 (7), 2262–2266.
- 121 Heo, J. H.; Han, H. J.; Kim, D.; Ahn, T. K.; Im, S. H. Hysteresis-Less Inverted CH₃NH₃PbI₃ Planar Perovskite Hybrid Solar Cells with 18.1% Power Conversion Efficiency. *Energy Environ. Sci.* **2015**, *8* (5), 1602–1608.
- 122 Shi, Y.; Rojas-Gatjens, E.; Wang, J.; Pothoof, J.; Giridharagopal, R.; Ho, K.; Jiang, F.; Taddei, M.; Yang, Z.; Sanehira, E. M.; Irwin, M. D.; Silva-Acuña, C.; Ginger, D.

S. (3-Aminopropyl)Trimethoxysilane Surface Passivation Improves Perovskite Solar Cell Performance by Reducing Surface Recombination Velocity. *ACS Energy Lett.* **2022**, 4081–4088.

- 123 Jung, S. K.; Lee, D. S.; Ann, M. H.; Im, S. H.; Kim, J. H.; Kwon, O. P. Non-Fullerene Organic Electron-Transporting Materials for Perovskite Solar Cells. *ChemSusChem* 2018, 11 (22), 3882–3892.
- Warby, J.; Zu, F.; Zeiske, S.; Gutierrez-partida, E.; Frohloff, L.; Frohna, K.; Mosconi, E.; Radicchi, E.; Lang, F.; Shah, S.; Peña-, F.; Hempel, H.; Unold, T.; Koch, N.; Armin, A.; Angelis, F. De; Stranks, S.; Neher, D.; Stolterfoht, M. Understanding Performance Limiting Interfacial Recombination in Pin Perovskite Solar Cells. *Accept. Adv. Energy Mater.* 2022, 2103567, 1–10.
- 125 Wojciechowski, K.; Ramirez, I.; Gorisse, T.; Dautel, O.; Dasari, R.; Sakai, N.; Hardigree, J. M.; Song, S.; Marder, S.; Riede, M.; Wantz, G.; Snaith, H. J. Cross-Linkable Fullerene Derivatives for Solution-Processed n-i-p Perovskite Solar Cells. ACS Energy Lett. 2016, 1 (4), 648–653.
- Bai, Y.; Dong, Q.; Shao, Y.; Deng, Y.; Wang, Q.; Shen, L.; Wang, D.; Wei, W.; Huang, J. Enhancing Stability and Efficiency of Perovskite Solar Cells with Crosslinkable Silane-Functionalized and Doped Fullerene. *Nat. Commun.* 2016, 7, 1–9.
- 127 Jiang, K.; Wu, F.; Zhu, L.; Yan, H. Naphthodiperylenetetraimide-Based Polymer as Electron-Transporting Material for Efficient Inverted Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* **2018**, *10* (42), 36549–36555.
- 128 Chen, C.; Cheng, M.; Li, H.; Qiao, F.; Liu, P.; Li, H.; Kloo, L.; Sun, L. Molecular Engineering of Ionic Type Perylenediimide Dimer-Based Electron Transport Materials for Efficient Planar Perovskite Solar Cells. *Mater. Today Energy* 2018, 9, 264–270.
- 129 Jung, S. K.; Heo, J. H.; Lee, D. W.; Lee, S. H.; Lee, S. C.; Yoon, W.; Yun, H.; Kim, D.; Kim, J. H.; Im, S. H.; Kwon, O. P. Homochiral Asymmetric-Shaped Electron-Transporting Materials for Efficient Non-Fullerene Perovskite Solar Cells. *ChemSusChem* 2019, 12 (1), 224–230.
- Jung, S. K.; Heo, J. H.; Lee, D. W.; Lee, S. C.; Lee, S. H.; Yoon, W.; Yun, H.; Im, S. H.; Kim, J. H.; Kwon, O. P. Nonfullerene Electron Transporting Material Based on Naphthalene Diimide Small Molecule for Highly Stable Perovskite Solar Cells with Efficiency Exceeding 20%. Adv. Funct. Mater. 2018, 28 (20).
- 131 Kim, H. II; Kim, M. J.; Choi, K.; Lim, C.; Kim, Y. H.; Kwon, S. K.; Park, T. Improving the Performance and Stability of Inverted Planar Flexible Perovskite Solar Cells Employing a Novel NDI-Based Polymer as the Electron Transport Layer. *Adv. Energy Mater.* 2018, 8 (16), 1–7.
- 132 Zhu, Z.; Zhao, D.; Chueh, C. C.; Shi, X.; Li, Z.; Jen, A. K. Y. Highly Efficient and Stable Perovskite Solar Cells Enabled by All-Crosslinked Charge-Transporting Layers. *Joule* **2018**, *2* (1), 168–183.
- 133 Zhao, D.; Zhu, Z.; Kuo, M. Y.; Chueh, C. C.; Jen, A. K. Y. Hexaazatrinaphthylene Derivatives: Efficient Electron-Transporting Materials with Tunable Energy Levels for Inverted Perovskite Solar Cells. *Angew. Chemie - Int. Ed.* **2016**, *55* (31), 8999– 9003.

- 134 Quinn, J. T. E.; Zhu, J.; Li, X.; Wang, J.; Li, Y. Recent Progress in the Development of N-Type Organic Semiconductors for Organic Field Effect Transistors. *J. Mater. Chem. C* 2017, 5 (34), 8654–8681.
- 135 Bhosale, S. V.; Jani, C. H.; Langford, S. J. Chemistry of Naphthalene Diimides. *Chem. Soc. Rev.* **2008**, *37* (2), 331–342.
- Nowak-Król, A.; Shoyama, K.; Stolte, M.; Würthner, F. Naphthalene and Perylene Diimides-Better Alternatives to Fullerenes for Organic Electronics? *Chem. Commun.* 2018, 54 (98), 13763–13772.
- 137 Li, F.; Deng, X.; Qi, F.; Li, Z.; Liu, D.; Shen, D.; Qin, M.; Wu, S.; Lin, F.; Jang, S. H.; Zhang, J.; Lu, X.; Lei, D.; Lee, C. S.; Zhu, Z.; Jen, A. K. Y. Regulating Surface Termination for Efficient Inverted Perovskite Solar Cells with Greater Than 23% Efficiency. J. Am. Chem. Soc. 2020, 142 (47), 20134–20142.
- Heo, J. H.; Im, S. H.; Noh, J. H.; Mandal, T. N.; Lim, C. S.; Chang, J. A.; Lee, Y. H.; Kim, H. J.; Sarkar, A.; Nazeeruddin, M. K.; Grätzel, M.; Seok, S. II. Efficient Inorganic-Organic Hybrid Heterojunction Solar Cells Containing Perovskite Compound and Polymeric Hole Conductors. *Nat. Photonics* 2013, 7 (6), 486–491.
- 139 Zhao, D.; Sexton, M.; Park, H. Y.; Baure, G.; Nino, J. C.; So, F. High-Efficiency Solution-Processed Planar Perovskite Solar Cells with a Polymer Hole Transport Layer. Adv. Energy Mater. 2015, 5 (6), 1–5.
- 140 Liu, D.; Li, Y.; Yuan, J.; Hong, Q.; Shi, G.; Yuan, D.; Wei, J.; Huang, C.; Tang, J.; Fung, M. K. Improved Performance of Inverted Planar Perovskite Solar Cells with F4-TCNQ Doped PEDOT:PSS Hole Transport Layers. *J. Mater. Chem. A* 2017, *5* (12), 5701–5708.
- 141 Jung, E. H.; Jeon, N. J.; Park, E. Y.; Moon, C. S.; Shin, T. J.; Yang, T. Y.; Noh, J. H.; Seo, J. Efficient, Stable and Scalable Perovskite Solar Cells Using Poly(3-Hexylthiophene). *Nature* 2019, 567 (7749), 511–515.
- 142 Tremblay, M. H.; Schutt, K.; Zhang, Y.; Lim, J.; Lin, Y. H.; Warby, J. H.; Barlow, S.; Snaith, H. J.; Marder, S. R. A Photo-Crosslinkable Bis-Triarylamine Side-Chain Polymer as a Hole-Transport Material for Stable Perovskite Solar Cells. *Sustain. Energy Fuels* 2019, 4 (1), 190–198.
- 143 Zuniga, C. A.; Barlow, S.; Marder, S. R. Approaches to Solution-Processed Multilayer Organic Light-Emitting Diodes Based on Cross-Linking. *Chem. Mater.* 2011, 23 (3), 658–681.
- Zhang, Y. D.; Hreha, R. D.; Jabbour, G. E.; Kippelen, B.; Peyghambarian, N.; Marder, S. R. Photo-Crosslinkable Polymers as Hole-Transport Materials for Organic Light-Emitting Diodes. J. Mater. Chem. 2002, 12 (6), 1703–1708.
- 145 Sung, S. J.; Cho, K. Y.; Hah, H.; Lee, J.; Shim, H. K.; Park, J. K. Two Different Reaction Mechanisms of Cinnamate Side Groups Attached to the Various Polymer Backbones. *Polymer (Guildf)*. **2006**, *47* (7), 2314–2321.
- Al Kurdi, K.; McCarthy, D. P.; McMeekin, D. P.; Furer, S. O.; Tremblay, M. H.; Barlow, S.; Bach, U.; Marder, S. R. A Naphthalene Diimide Side-Chain Polymer as an Electron-Extraction Layer for Stable Perovskite Solar Cells. *Mater. Chem. Front.* 2021, 5 (1), 450–457.
- 147 Un, H. I.; Gregory, S. A.; Mohapatra, S. K.; Xiong, M.; Longhi, E.; Lu, Y.; Rigin, S.; Jhulki, S.; Yang, C. Y.; Timofeeva, T. V.; Wang, J. Y.; Yee, S. K.; Barlow, S.; Marder,

S. R.; Pei, J. Understanding the Effects of Molecular Dopant on N-Type Organic Thermoelectric Properties. *Adv. Energy Mater.* **2019**, *9* (24), 1–10.

- 148 Kim, M. J.; Lee, M.; Min, H.; Kim, S.; Yang, J.; Kweon, H.; Lee, W.; Kim, D. H.; Choi, J. H.; Ryu, D. Y.; Kang, M. S.; Kim, B. S.; Cho, J. H. Universal Three-Dimensional Crosslinker for All-Photopatterned Electronics. *Nat. Commun.* 2020, *11* (1), 1–11.
- 149 Guo, Y.; Sato, W.; Inoue, K.; Zhang, W.; Yu, G.; Nakamura, E. N-Type Doping for Efficient Polymeric Electron-Transporting Layers in Perovskite Solar Cells. J. Mater. Chem. A 2016, 4 (48), 18852–18856.
- Chen, H.; Maxwell, A.; Li, C.; Teale, S.; Chen, B.; Zhu, T.; Ugur, E.; Harrison, G.; Grater, L.; Wang, J.; Wang, Z.; Zeng, L.; Park, S. M.; Chen, L.; Serles, P.; Awni, R. A.; Subedi, B.; Zheng, X.; Xiao, C.; Podraza, N. J.; Filleter, T.; Liu, C.; Yang, Y.; Luther, J. M.; De Wolf, S.; Kanatzidis, M. G.; Yan, Y.; Sargent, E. H. Regulating Surface Potential Maximizes Voltage in All-Perovskite Tandems. *Nature* 2023, *613* (7945), 676–681.
- Fürer, S. O.; Rietwyk, K. J.; Pulvirenti, F.; McMeekin, D. P.; Surmiak, M. A.; Raga, S. R.; Mao, W.; Lin, X.; Hora, Y.; Wang, J.; Shi, Y.; Barlow, S.; Ginger, D. S.; Marder, S. R.; Bach, U. Naphthalene-Imide Self-Assembled Monolayers as a Surface Modification of ITO for Improved Thermal Stability of Perovskite Solar Cells. ACS Appl. Energy Mater. 2023, 6 (2), 667–677.
- 152 Burgelman, M.; Decock, K.; Khelifi, S.; Abass, A. Advanced Electrical Simulation of Thin Film Solar Cells. *Thin Solid Films* **2013**, *535* (1), 296–301.
- 153 Burgelman, M.; Nollet, P.; Degrave, S. Modelling Polycrystalline Semiconductor Solar Cells. *Thin Solid Films* **2000**, *361*, 527–532.
- Taddei, M.; Smith, J. A.; Gallant, B. M.; Zhou, S.; Westbrook, R. J. E.; Shi, Y.; Wang, J.; Drysdale, J. N.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Snaith, H. J.; Ginger, D. S. Ethylenediamine Addition Improves Performance and Suppresses Phase Instabilities in Mixed-Halide Perovskites. 2022, 7(12), 4265-4273.
- Jin, H.; Farrar, M. D.; Ball, J. M.; Dasgupta, A.; Caprioglio, P.; Narayanan, S.; Oliver, R. D. J.; Rombach, F. M.; Putland, B. W. J.; Johnston, M. B.; Snaith, H. J. Alumina Nanoparticle Interfacial Buffer Layer for Low-Bandgap Lead-in Perovskite Solar Cells. *Adv. Funct. Mater.* 2023.
- 156 Lee, J.; Baik, S. Enhanced Crystallinity of CH₃NH₃PbI₃ by the Pre-Coordination of PbI₂-DMSO Powders for Highly Reproducible and Efficient Planar Heterojunction Perovskite Solar Cells. *RSC Adv.* **2018**, *8* (2), 1005–1013.
- 157 Saliba, M.; Correa-Baena, J. P.; Grätzel, M.; Hagfeldt, A.; Abate, A. Perovskite Solar Cells: From the Atomic Level to Film Quality and Device Performance. *Angew. Chemie - Int. Ed.* **2018**, *57* (10), 2554–2569.
- 158 Jariwala, S.; Sun, H.; Adhyaksa, G. W. P.; Lof, A.; Muscarella, L. A.; Ehrler, B.; Garnett, E. C.; Ginger, D. S. Local Crystal Misorientation Influences Non-Radiative Recombination in Halide Perovskites. *Joule* 2019, *3* (12), 3048–3060.
- 159 Valverde-Chávez, D. A.; Rojas-Gatjens, E.; Williamson, J.; Jariwala, S.; Shi, Y.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Ginger, D. S.; Silva-Acuña, C. Nonlinear Photocarrier Dynamics and the Role of Shallow Traps in Mixed-Halide Mixed-Cation Hybrid Perovskites. J. Mater. Chem. C 2021, 9 (26), 8204–8212.

- 160 Pothoof, J.; Westbrook, R. J. E.; Giridharagopal, R.; Breshears, M. D.; Ginger, D. S. Surface Passivation Suppresses Local Ion Motion in Halide Perovskites. *J. Phys. Chem. Lett.* **2023**, 6092–6098.
- 161 Jena, A. K.; Numata, Y.; Ikegami, M.; Miyasaka, T. Role of Spiro-OMeTAD in Performance Deterioration of Perovskite Solar Cells at High Temperature and Reuse of the Perovskite Films to Avoid Pb-Waste. J. Mater. Chem. A 2018, 6 (5), 2219– 2230.
- 162 Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T., Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. J. Am. Chem. Soc. 2009, 131 (17), 6050-6051.
- 163 Park, N.-G., Perovskite solar cells: an emerging photovoltaic technology. *Mater. Today* **2015**, *18* (2), 65-72.
- 164 Snaith, H. J., Present status and future prospects of perovskite photovoltaics. *Nature Materials* **2018**, *17* (5), 372-376.
- Jena, A. K.; Kulkarni, A.; Miyasaka, T., Halide Perovskite Photovoltaics:
 Background, Status, and Future Prospects. *Chem. Rev.* 2019, *119* (5), 3036-3103.
- 166 Mitzi, D. B., Introduction: Perovskites. *Chem. Rev.* **2019**, *119* (5), 3033-3035.
- 167 Faridi, A. W.; Imran, M.; Tariq, G. H.; Ullah, S.; Noor, S. F.; Ansar, S.; Sher, F., Synthesis and Characterization of High-Efficiency Halide Perovskite Nanomaterials for Light-Absorbing Applications. *Industrial & Engineering Chemistry Research* 2023, 62 (11), 4494-4502.
- 168 Miyata, A.; Mitioglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J., Direct measurement of the exciton binding energy and effective masses for charge carriers in organic–inorganic tri-halide perovskites. *Nature Physics* 2015, *11* (7), 582-587.
- 169 Adhyaksa, G. W. P.; Veldhuizen, L. W.; Kuang, Y.; Brittman, S.; Schropp, R. E. I.; Garnett, E. C., Carrier Diffusion Lengths in Hybrid Perovskites: Processing, Composition, Aging, and Surface Passivation Effects. *Chem. Mater.* 2016, 28 (15), 5259-5263.
- 170 De Wolf, S.; Holovsky, J.; Moon, S.-J.; Löper, P.; Niesen, B.; Ledinsky, M.; Haug, F.-J.; Yum, J.-H.; Ballif, C., Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. *The Journal of Physical Chemistry Letters* 2014, 5 (6), 1035-1039.
- Oliver, R. D. J.; Caprioglio, P.; Peña-Camargo, F.; Buizza, L. R. V.; Zu, F.; Ramadan, A. J.; Motti, S. G.; Mahesh, S.; McCarthy, M. M.; Warby, J. H.; Lin, Y.-H.; Koch, N.; Albrecht, S.; Herz, L. M.; Johnston, M. B.; Neher, D.; Stolterfoht, M.; Snaith, H. J., Understanding and suppressing non-radiative losses in methylammonium-free wide-bandgap perovskite solar cells. *Energy & Environmental Science* 2022, *15* (2), 714-726.
- 172 McCluskey, M. D.; Janotti, A., Defects in Semiconductors. J. Appl. Phys. 2020, 127 (19), 190401.
- 173 Kim, G.-W.; Petrozza, A., Defect Tolerance and Intolerance in Metal-Halide Perovskites. *Adv. Energy Mater.* **2020**, *10* (37), 2001959.
- 174 Bera, S.; Saha, A.; Mondal, S.; Biswas, A.; Mallick, S.; Chatterjee, R.; Roy, S., Review of defect engineering in perovskites for photovoltaic application. *Materials Advances* **2022**, *3* (13), 5234-5247.

- Pradhan, R. R.; Eswaran, M. K.; Subbiah, A. S.; Babayigit, A.; De Wolf, S.;
 Schwingenschlögl, U., Elucidating the Role of Contact-Induced Gap States and
 Passivation Molecules at Perovskite/Metal Contacts. ACS Applied Energy Materials
 2023, 6 (8), 4111-4118.
- Warby, J.; Zu, F.; Zeiske, S.; Gutierrez-Partida, E.; Frohloff, L.; Kahmann, S.;
 Frohna, K.; Mosconi, E.; Radicchi, E.; Lang, F.; Shah, S.; Peña-Camargo, F.;
 Hempel, H.; Unold, T.; Koch, N.; Armin, A.; De Angelis, F.; Stranks, S. D.; Neher,
 D.; Stolterfoht, M., Understanding Performance Limiting Interfacial Recombination
 in pin Perovskite Solar Cells. *Adv. Energy Mater.* 2022, *12* (12), 2103567.
- Ye, J.; Byranvand, M. M.; Martínez, C. O.; Hoye, R. L. Z.; Saliba, M.; Polavarapu, L., Defect Passivation in Lead-Halide Perovskite Nanocrystals and Thin Films: Toward Efficient LEDs and Solar Cells. *Angew. Chem. Int. Ed.* 2021, *60* (40), 21636-21660.
- 178 Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J., Surface passivation of perovskite film for efficient solar cells. *Nature Photonics* **2019**, *13* (7), 460-466.
- 179 Perini, C. A. R.; Rojas-Gatjens, E.; Ravello, M.; Castro-Mendez, A.-F.; Hidalgo, J.; An, Y.; Kim, S.; Lai, B.; Li, R.; Silva-Acuña, C.; Correa-Baena, J.-P., Interface Reconstruction from Ruddlesden–Popper Structures Impacts Stability in Lead Halide Perovskite Solar Cells. *Adv. Mater.* 2022, *34* (51), 2204726.
- 180 Cho, Y.; Soufiani, A. M.; Yun, J. S.; Kim, J.; Lee, D. S.; Seidel, J.; Deng, X.; Green, M. A.; Huang, S.; Ho-Baillie, A. W. Y., Mixed 3D–2D Passivation Treatment for Mixed-Cation Lead Mixed-Halide Perovskite Solar Cells for Higher Efficiency and Better Stability. *Adv. Energy Mater.* 2018, 8 (20), 1703392.
- 181 Wang, F.; Geng, W.; Zhou, Y.; Fang, H.-H.; Tong, C.-J.; Loi, M. A.; Liu, L.-M.; Zhao, N., Phenylalkylamine Passivation of Organolead Halide Perovskites Enabling High-Efficiency and Air-Stable Photovoltaic Cells. *Adv. Mater.* 2016, 28 (45), 9986-9992.
- Shi, Y.; Rojas-Gatjens, E.; Wang, J.; Pothoof, J.; Giridharagopal, R.; Ho, K.; Jiang, F.; Taddei, M.; Yang, Z.; Sanehira, E. M.; Irwin, M. D.; Silva-Acuña, C.; Ginger, D. S., (3-Aminopropyl)trimethoxysilane Surface Passivation Improves Perovskite Solar Cell Performance by Reducing Surface Recombination Velocity. *ACS Energy Letters* 2022, 7 (11), 4081-4088.
- 183 Taddei, M.; Smith, J. A.; Gallant, B. M.; Zhou, S.; Westbrook, R. J. E.; Shi, Y.; Wang, J.; Drysdale, J. N.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Snaith, H. J.; Ginger, D. S., Ethylenediamine Addition Improves Performance and Suppresses Phase Instabilities in Mixed-Halide Perovskites. ACS Energy Letters 2022, 4265-4273.
- Jiang, Q.; Tong, J.; Xian, Y.; Kerner, R. A.; Dunfield, S. P.; Xiao, C.; Scheidt, R. A.; Kuciauskas, D.; Wang, X.; Hautzinger, M. P.; Tirawat, R.; Beard, M. C.; Fenning, D. P.; Berry, J. J.; Larson, B. W.; Yan, Y.; Zhu, K., Surface reaction for efficient and stable inverted perovskite solar cells. *Nature* 2022, *611* (7935), 278-283.
- 185 Noel, N. K.; Abate, A.; Stranks, S. D.; Parrott, E. S.; Burlakov, V. M.; Goriely, A.; Snaith, H. J., Enhanced Photoluminescence and Solar Cell Performance via Lewis Base Passivation of Organic–Inorganic Lead Halide Perovskites. ACS Nano 2014, 8 (10), 9815-9821.

- Abate, A.; Saliba, M.; Hollman, D. J.; Stranks, S. D.; Wojciechowski, K.; Avolio, R.; Grancini, G.; Petrozza, A.; Snaith, H. J., Supramolecular Halogen Bond Passivation of Organic–Inorganic Halide Perovskite Solar Cells. *Nano Lett.* 2014, *14* (6), 3247-3254.
- 187 Akman, E.; Shalan, A. E.; Sadegh, F.; Akin, S., Moisture-Resistant FAPbI3 Perovskite Solar Cell with 22.25 % Power Conversion Efficiency through Pentafluorobenzyl Phosphonic Acid Passivation. *ChemSusChem* 2021, 14 (4), 1176-1183.
- 188 Yang, S.; Dai, J.; Yu, Z.; Shao, Y.; Zhou, Y.; Xiao, X.; Zeng, X. C.; Huang, J., Tailoring Passivation Molecular Structures for Extremely Small Open-Circuit Voltage Loss in Perovskite Solar Cells. J. Am. Chem. Soc. 2019, 141 (14), 5781-5787.
- 189 Lee, S.-H.; Jeong, S.; Seo, S.; Shin, H.; Ma, C.; Park, N.-G., Acid Dissociation Constant: A Criterion for Selecting Passivation Agents in Perovskite Solar Cells. ACS Energy Letters 2021, 6 (4), 1612-1621.
- 190 Park, S. M.; Wei, M.; Xu, J.; Atapattu, H. R.; Eickemeyer, F. T.; Darabi, K.; Grater, L.; Yang, Y.; Liu, C.; Teale, S.; Chen, B.; Chen, H.; Wang, T.; Zeng, L.; Maxwell, A.; Wang, Z.; Rao, K. R.; Cai, Z.; Zakeeruddin, S. M.; Pham, J. T.; Risko, C. M.; Amassian, A.; Kanatzidis, M. G.; Graham, K. R.; Grätzel, M.; Sargent, E. H., Engineering ligand reactivity enables high-temperature operation of stable perovskite solar cells. *Science* **2023**, *381* (6654), 209-215.
- 191 Chen, H.-C.; Lan, J.-M.; Hsu, H.-L.; Li, C.-W.; Shieh, T.-S.; Wong, K.-T.; Chen, C.-P., Synergistic improvements in the performance and stability of inverted planar MAPbI3-based perovskite solar cells incorporating benzylammonium halide salt additives. *Materials Chemistry Frontiers* 2021, 5 (8), 3378-3387.
- 192 Jariwala, S.; Burke, S.; Dunfield, S.; Shallcross, R. C.; Taddei, M.; Wang, J.; Eperon, G. E.; Armstrong, N. R.; Berry, J. J.; Ginger, D. S., Reducing Surface Recombination Velocity of Methylammonium-Free Mixed-Cation Mixed-Halide Perovskites via Surface Passivation. *Chem. Mater.* 2021, *33* (13), 5035-5044.
- 193 Oliver, R. D. J.; Lin, Y.-H.; Horn, A. J.; Xia, C. Q.; Warby, J. H.; Johnston, M. B.; Ramadan, A. J.; Snaith, H. J., Thermally Stable Passivation toward High Efficiency Inverted Perovskite Solar Cells. ACS Energy Letters 2020, 5 (11), 3336-3343.
- Alanazi, A. Q.; Almalki, M. H.; Mishra, A.; Kubicki, D. J.; Wang, Z.; Merten, L.;
 Eickemeyer, F. T.; Zhang, H.; Ren, D.; Alyamani, A. Y.; Albrithen, H.; Albadri, A.;
 Alotaibi, M. H.; Hinderhofer, A.; Zakeeruddin, S. M.; Schreiber, F.; Hagfeldt, A.;
 Emsley, L.; Milić, J. V.; Graetzel, M., Benzylammonium-Mediated Formamidinium
 Lead Iodide Perovskite Phase Stabilization for Photovoltaics. *Adv. Funct. Mater.*2021, *31* (30).
- Tan, S.; Huang, T.; Yavuz, I.; Wang, R.; Weber, M. H.; Zhao, Y.; Abdelsamie, M.;
 Liao, M. E.; Wang, H.-C.; Huynh, K.; Wei, K.-H.; Xue, J.; Babbe, F.; Goorsky, M.
 S.; Lee, J.-W.; Sutter-Fella, C. M.; Yang, Y., Surface Reconstruction of Halide
 Perovskites During Post-treatment. J. Am. Chem. Soc. 2021, 143 (18), 6781-6786.
- 196 Smith, I. C.; Hoke, E. T.; Solis-Ibarra, D.; McGehee, M. D.; Karunadasa, H. I., A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability. *Angew. Chem. Int. Ed.* 2014, *53* (42), 11232-11235.

- Mohanty, A. D.; Bae, C., Mechanistic analysis of ammonium cation stability for alkaline exchange membrane fuel cells. *Journal of Materials Chemistry A* 2014, 2 (41), 17314-17320.
- 198 Gibson, H. W.; Jones, J. W.; Zakharov, L. N.; Rheingold, A. L.; Slebodnick, C., Complexation Equilibria Involving Salts in Non-Aqueous Solvents: Ion Pairing and Activity Considerations. *Chemistry – A European Journal* **2011**, *17* (11), 3192-3206.
- Conings, B.; Drijkoningen, J.; Gauquelin, N.; Babayigit, A.; D'Haen, J.;
 D'Olieslaeger, L.; Ethirajan, A.; Verbeeck, J.; Manca, J.; Mosconi, E.; Angelis, F.
 D.; Boyen, H.-G., Intrinsic Thermal Instability of Methylammonium Lead Trihalide
 Perovskite. *Adv. Energy Mater.* 2015, 5 (15), 1500477.
- Mahesh, S.; Ball, J. M.; Oliver, R. D. J.; McMeekin, D. P.; Nayak, P. K.; Johnston, M. B.; Snaith, H. J., Revealing the origin of voltage loss in mixed-halide perovskite solar cells. *Energy & Environmental Science* 2020, *13* (1), 258-267.
- 201 Peña-Camargo, F.; Caprioglio, P.; Zu, F.; Gutierrez-Partida, E.; Wolff, C. M.; Brinkmann, K.; Albrecht, S.; Riedl, T.; Koch, N.; Neher, D.; Stolterfoht, M., Halide Segregation versus Interfacial Recombination in Bromide-Rich Wide-Gap Perovskite Solar Cells. ACS Energy Letters 2020, 5 (8), 2728-2736.
- 202 Xia, X.; Wu, W.; Li, H.; Zheng, B.; Xue, Y.; Xu, J.; Zhang, D.; Gao, C.; Liu, X., Spray reaction prepared FA1–xCsxPbI3 solid solution as a light harvester for perovskite solar cells with improved humidity stability. *RSC Advances* 2016, 6 (18), 14792-14798.
- 203 Sutton, R. J.; Eperon, G. E.; Miranda, L.; Parrott, E. S.; Kamino, B. A.; Patel, J. B.; Hörantner, M. T.; Johnston, M. B.; Haghighirad, A. A.; Moore, D. T.; Snaith, H. J., Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. *Adv. Energy Mater.* **2016**, *6* (8), 1502458.
- 204 Tao, S.; Schmidt, I.; Brocks, G.; Jiang, J.; Tranca, I.; Meerholz, K.; Olthof, S., Absolute energy level positions in tin- and lead-based halide perovskites. *Nature Communications* **2019**, *10* (1), 2560.
- 205 Kim, J.; Saidaminov, M. I.; Tan, H.; Zhao, Y.; Kim, Y.; Choi, J.; Jo, J. W.; Fan, J.; Quintero-Bermudez, R.; Yang, Z.; Quan, L. N.; Wei, M.; Voznyy, O.; Sargent, E. H., Amide-Catalyzed Phase-Selective Crystallization Reduces Defect Density in Wide-Bandgap Perovskites. *Adv. Mater.* 2018, *30* (13), 1706275.
- 206 Jariwala, S.; Sun, H.; Adhyaksa, G. W. P.; Lof, A.; Muscarella, L. A.; Ehrler, B.; Garnett, E. C.; Ginger, D. S., Local Crystal Misorientation Influences Non-radiative Recombination in Halide Perovskites. *Joule* 2019, *3* (12), 3048-3060.
- 207 Wang, J.; Fu, W.; Jariwala, S.; Sinha, I.; Jen, A. K. Y.; Ginger, D. S., Reducing Surface Recombination Velocities at the Electrical Contacts Will Improve Perovskite Photovoltaics. *ACS Energy Letters* **2019**, *4* (1), 222-227.
- 208 Alanazi, A. Q.; Almalki, M. H.; Mishra, A.; Kubicki, D. J.; Wang, Z.; Merten, L.; Eickemeyer, F. T.; Zhang, H.; Ren, D.; Alyamani, A. Y.; Albrithen, H.; Albadri, A.; Alotaibi, M. H.; Hinderhofer, A.; Zakeeruddin, S. M.; Schreiber, F.; Hagfeldt, A.; Emsley, L.; Milić, J. V.; Graetzel, M., Benzylammonium-Mediated Formamidinium Lead Iodide Perovskite Phase Stabilization for Photovoltaics. *Adv. Funct. Mater.* 2021, *31* (30), 2101163.
- 209 Yang, X.; Fu, Y.; Su, R.; Zheng, Y.; Zhang, Y.; Yang, W.; Yu, M.; Chen, P.; Wang, Y.; Wu, J.; Luo, D.; Tu, Y.; Zhao, L.; Gong, Q.; Zhu, R., Superior Carrier Lifetimes

Exceeding 6 µs in Polycrystalline Halide Perovskites. *Adv. Mater.* **2020**, *32* (39), 2002585.

- 210 Guo, Y.; Li, X.; Kang, L.; Cheng, C.; He, X.; Liu, X.; Liu, J.; Li, Y.; Dong, C., Mechanistic Understanding of Cetyltrimethylammonium Bromide-Assisted Durable CH3NH3PbI3 Film for Stable ZnO-Based Perovskite Solar Cells. ACS Applied Energy Materials 2020, 3 (10), 9856-9865.
- 211 Wang, S.; Zhu, Y.; Wang, C.; Ma, R., Interface modification by a multifunctional ammonium salt for high performance and stable planar perovskite solar cells. *Journal of Materials Chemistry A* **2019**, *7* (19), 11867-11876.
- 212 Al-Ashouri, A.; Magomedov, A.; Roß, M.; Jošt, M.; Talaikis, M.; Chistiakova, G.; Bertram, T.; Márquez, J. A.; Köhnen, E.; Kasparavičius, E.; Levcenco, S.; Gil-Escrig, L.; Hages, C. J.; Schlatmann, R.; Rech, B.; Malinauskas, T.; Unold, T.; Kaufmann, C. A.; Korte, L.; Niaura, G.; Getautis, V.; Albrecht, S., Conformal monolayer contacts with lossless interfaces for perovskite single junction and monolithic tandem solar cells. *Energy & Environmental Science* **2019**, *12* (11), 3356-3369.
- Al-Ashouri, A.; Köhnen, E.; Li, B.; Magomedov, A.; Hempel, H.; Caprioglio, P.; Márquez, J. A.; Morales Vilches, A. B.; Kasparavicius, E.; Smith, J. A.; Phung, N.; Menzel, D.; Grischek, M.; Kegelmann, L.; Skroblin, D.; Gollwitzer, C.; Malinauskas, T.; Jošt, M.; Matič, G.; Rech, B.; Schlatmann, R.; Topič, M.; Korte, L.; Abate, A.; Stannowski, B.; Neher, D.; Stolterfoht, M.; Unold, T.; Getautis, V.; Albrecht, S., Monolithic perovskite/silicon tandem solar cell with >29% efficiency by enhanced hole extraction. *Science* 2020, *370* (6522), 1300-1309.
- 214 Schultes, M.; Giesbrecht, N.; Küffner, J.; Ahlswede, E.; Docampo, P.; Bein, T.; Powalla, M., Universal Nanoparticle Wetting Agent for Upscaling Perovskite Solar Cells. ACS Applied Materials & Interfaces 2019, 11 (13), 12948-12957.
- 215 Mitzi, D. B., Introduction: Perovskites. *Chem. Rev.* **2019**, *119* (5), 3033-3035.
- 216 Stoumpos, C. C.; Kanatzidis, M. G., The Renaissance of Halide Perovskites and Their Evolution as Emerging Semiconductors. *Acc. Chem. Res.* **2015**, *48* (10), 2791-2802.
- 217 Lee, M. V.; Raga, S. R.; Kato, Y.; Leyden, M. R.; Ono, L. K.; Wang, S.; Qi, Y., Transamidation of dimethylformamide during alkylammonium lead triiodide film formation for perovskite solar cells. *J. Mater. Res.* **2017**, *32* (1), 45-55.
- 218 Dou, B.; Wheeler, L. M.; Christians, J. A.; Moore, D. T.; Harvey, S. P.; Berry, J. J.; Barnes, F. S.; Shaheen, S. E.; van Hest, M. F. A. M., Degradation of Highly Alloyed Metal Halide Perovskite Precursor Inks: Mechanism and Storage Solutions. ACS Energy Letters 2018, 3 (4), 979-985.
- 219 Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Grätzel, M., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy & Environmental Science* **2016**, *9* (6), 1989-1997.
- 220 Jariwala, S.; Kumar, R. E.; Eperon, G. E.; Shi, Y.; Fenning, D. P.; Ginger, D. S., Dimethylammonium Addition to Halide Perovskite Precursor Increases Vertical and Lateral Heterogeneity. ACS Energy Letters 2022, 7 (1), 204-210.
- 221 Eperon, G. E.; Stone, K. H.; Mundt, L. E.; Schloemer, T. H.; Habisreutinger, S. N.; Dunfield, S. P.; Schelhas, L. T.; Berry, J. J.; Moore, D. T., The Role of
Dimethylammonium in Bandgap Modulation for Stable Halide Perovskites. *ACS Energy Letters* **2020**, *5* (6), 1856-1864.

- 222 McMeekin, D. P.; Holzhey, P.; Fürer, S. O.; Harvey, S. P.; Schelhas, L. T.; Ball, J. M.; Mahesh, S.; Seo, S.; Hawkins, N.; Lu, J.; Johnston, M. B.; Berry, J. J.; Bach, U.; Snaith, H. J., Intermediate-phase engineering via dimethylammonium cation additive for stable perovskite solar cells. *Nature Materials* **2023**, *22* (1), 73-83.
- 223 Van Gompel, W. T. M.; Herckens, R.; Reekmans, G.; Ruttens, B.; D'Haen, J.; Adriaensens, P.; Lutsen, L.; Vanderzande, D., Degradation of the Formamidinium Cation and the Quantification of the Formamidinium–Methylammonium Ratio in Lead Iodide Hybrid Perovskites by Nuclear Magnetic Resonance Spectroscopy. *The Journal of Physical Chemistry C* 2018, *122* (8), 4117-4124.
- Kerner, R. A.; Schloemer, T. H.; Schulz, P.; Berry, J. J.; Schwartz, J.; Sellinger, A.; Rand, B. P., Amine additive reactions induced by the soft Lewis acidity of Pb2+ in halide perovskites. Part I: evidence for Pb–alkylamide formation. *Journal of Materials Chemistry C* 2019, 7 (18), 5251-5259.
- 225 Kerner, R. A.; Schloemer, T. H.; Schulz, P.; Berry, J. J.; Schwartz, J.; Sellinger, A.; Rand, B. P., Amine additive reactions induced by the soft Lewis acidity of Pb2+ in halide perovskites. Part II: impacts of amido Pb impurities in methylammonium lead triiodide thin films. *Journal of Materials Chemistry C* **2019**, 7 (18), 5244-5250.
- 226 Hu, J.; Kerner, R. A.; Pelczer, I.; Rand, B. P.; Schwartz, J., Organoammonium-Ionbased Perovskites Can Degrade to Pb0 via Amine–Pb(II) Coordination. *ACS Energy Letters* **2021**, *6* (6), 2262-2267.
- Xu, Y.; Xu, W.; Hu, Z.; Steele, J. A.; Wang, Y.; Zhang, R.; Zheng, G.; Li, X.; Wang, H.; Zhang, X.; Solano, E.; Roeffaers, M. B. J.; Uvdal, K.; Qing, J.; Zhang, W.; Gao, F., Impact of Amine Additives on Perovskite Precursor Aging: A Case Study of Light-Emitting Diodes. *The Journal of Physical Chemistry Letters* 2021, *12* (25), 5836-5843.
- 228 Dong, Q.; Shang, W.; Yu, X.; Yin, Y.; Jiang, C.; Feng, Y.; Bian, J.; Song, B.; Jin, S.; Zhou, Y.; Wang, L.; Shi, Y., Critical Role of Organoamines in the Irreversible Degradation of a Metal Halide Perovskite Precursor Colloid: Mechanism and Inhibiting Strategy. ACS Energy Letters 2022, 7 (1), 481-489.
- 229 Wang, X.; Fan, Y.; Wang, L.; Chen, C.; Li, Z.; Liu, R.; Meng, H.; Shao, Z.; Du, X.; Zhang, H.; Cui, G.; Pang, S., Perovskite Solution Aging: What Happened and How to Inhibit? *Chem* **2020**, *6* (6), 1369-1378.
- 230 Zhang, Y.; Xing, Z.; Fan, B.; Ni, Z.; Wang, F.; Hu, X.; Chen, Y., Uncovering Aging Chemistry of Perovskite Precursor Solutions and Anti-aging Mechanism of Additives. *Angew. Chem. Int. Ed.* 2023, 62 (8), e202215799.
- Valenzano, V.; Cesari, A.; Balzano, F.; Milella, A.; Fracassi, F.; Listorti, A.; Gigli, G.; Rizzo, A.; Uccello-Barretta, G.; Colella, S., Methylammonium-formamidinium reactivity in aged organometal halide perovskite inks. *Cell Reports Physical Science* 2021, 2 (5), 100432.
- 232 Kerner, R. A.; Schutt, K.; Zhu, K.; Berry, J. J., PbI2 Reagent Impurities Catalyze Mixed-Cation Halide Perovskite Ink Degradation. ACS Energy Letters 2022, 7 (12), 4333-4335.

- Hu, J.; Xu, Z.; Murrey, T. L.; Pelczer, I.; Kahn, A.; Schwartz, J.; Rand, B. P., Triiodide Attacks the Organic Cation in Hybrid Lead Halide Perovskites: Mechanism and Suppression. *Adv. Mater.* 2023, *35* (40), 2303373.
- Jiang, Q.; Tong, J.; Xian, Y.; Kerner, R. A.; Dunfield, S. P.; Xiao, C.; Scheidt, R. A.; Kuciauskas, D.; Wang, X.; Hautzinger, M. P.; Tirawat, R.; Beard, M. C.; Fenning, D. P.; Berry, J. J.; Larson, B. W.; Yan, Y.; Zhu, K., Surface reaction for efficient and stable inverted perovskite solar cells. *Nature* 2022, *611* (7935), 278-283.
- 235 Wang, M.; Shi, Z.; Fei, C.; Deng, Z. J. D.; Yang, G.; Dunfield, S. P.; Fenning, D. P.; Huang, J., Ammonium cations with high pKa in perovskite solar cells for improved high-temperature photostability. *Nature Energy* **2023**.
- Spanopoulos, I.; Ke, W.; Stoumpos, C. C.; Schueller, E. C.; Kontsevoi, O. Y.;
 Seshadri, R.; Kanatzidis, M. G., Unraveling the Chemical Nature of the 3D
 "Hollow" Hybrid Halide Perovskites. *J. Am. Chem. Soc.* 2018, *140* (17), 5728-5742.
- 237 Aoyagi, N.; Furusho, Y.; Sei, Y.; Endo, T., Fast equilibrium of zwitterionic adduct formation in reversible fixation–release system of CO2 by amidines under dry conditions. *Tetrahedron* **2013**, *69* (26), 5476-5480.
- 238 Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J., Surface passivation of perovskite film for efficient solar cells. *Nature Photonics* **2019**, *13* (7), 460-466.
- 239 Min, H.; Kim, M.; Lee, S.-U.; Kim, H.; Kim, G.; Choi, K.; Lee, J. H.; Seok, S. I., Efficient, stable solar cells by using inherent bandgap of α-phase formamidinium lead iodide. *Science* **2019**, *366* (6466), 749-753.
- 240 Perini, C. A. R.; Rojas-Gatjens, E.; Ravello, M.; Castro-Mendez, A.-F.; Hidalgo, J.; An, Y.; Kim, S.; Lai, B.; Li, R.; Silva-Acuña, C.; Correa-Baena, J.-P., Interface Reconstruction from Ruddlesden–Popper Structures Impacts Stability in Lead Halide Perovskite Solar Cells. *Adv. Mater.* 2022, *34* (51), 2204726.
- Shi, Y.; Rojas-Gatjens, E.; Wang, J.; Pothoof, J.; Giridharagopal, R.; Ho, K.; Jiang, F.; Taddei, M.; Yang, Z.; Sanehira, E. M.; Irwin, M. D.; Silva-Acuña, C.; Ginger, D. S., (3-Aminopropyl)trimethoxysilane Surface Passivation Improves Perovskite Solar Cell Performance by Reducing Surface Recombination Velocity. *ACS Energy Letters* 2022, 7 (11), 4081-4088.
- 242 Jariwala, S.; Burke, S.; Dunfield, S.; Shallcross, R. C.; Taddei, M.; Wang, J.; Eperon, G. E.; Armstrong, N. R.; Berry, J. J.; Ginger, D. S., Reducing Surface Recombination Velocity of Methylammonium-Free Mixed-Cation Mixed-Halide Perovskites via Surface Passivation. *Chem. Mater.* **2021**, *33* (13), 5035-5044.
- 243 Brown, D. J.; Evans, R. F., 100. Hydropyrimidines. Part I. 1,4,5,6-Tetrahydropyrimidine and its derivatives. *Journal of the Chemical Society* (*Resumed*) **1962**, (0), 527-533.
- 244 Grundmann, C.; Kreutzberger, A., Triazines. XIII. The Ring Cleavage of s-Triazine by Primary Amines. A New Method for the Synthesis of Heterocycles1,2. *J. Am. Chem. Soc.* **1955**, 77 (24), 6559-6562.
- 245 Suzuki, H.; Ohashi, M.; Itoh, K.; Matsuda, I.; Ishii, Y., Reaction of Group IV Organometallic Compounds. XXXII Modified Synthesis of Imidazolidines with N,N'-Bis(trimethylsilyl)-1,2-diamines. *Bull. Chem. Soc. Jpn.* **1975**, 48 (6), 1922-1924.

- 246 Taddei, M.; Smith, J. A.; Gallant, B. M.; Zhou, S.; Westbrook, R. J. E.; Shi, Y.; Wang, J.; Drysdale, J. N.; McCarthy, D. P.; Barlow, S.; Marder, S. R.; Snaith, H. J.; Ginger, D. S., Ethylenediamine Addition Improves Performance and Suppresses Phase Instabilities in Mixed-Halide Perovskites. ACS Energy Letters 2022, 4265-4273.
- 247 Knight, A. J.; Borchert, J.; Oliver, R. D. J.; Patel, J. B.; Radaelli, P. G.; Snaith, H. J.; Johnston, M. B.; Herz, L. M., Halide Segregation in Mixed-Halide Perovskites: Influence of A-Site Cations. ACS Energy Letters 2021, 6 (2), 799-808.
- 248 Hüttner, S.; Sommer, M.; Steiner, U.; Thelakkat, M., Organic field effect transistors from triarylamine side-chain polymers. *Appl. Phys. Lett.* **2010**, *96* (7), 073503.
- 249 Tremblay, M.-H.; Schutt, K.; Zhang, Y.; Lim, J.; Lin, Y.-H.; Warby, J. H.; Barlow, S.; Snaith, H. J.; Marder, S. R., A photo-crosslinkable bis-triarylamine side-chain polymer as a hole-transport material for stable perovskite solar cells. *Sustain. Energy Fuels* 2020, *4* (1), 190-198.
- 250 Pan, Z.; Peng, D.; Zhao, X.; Xu, W.; Bao, Y.; Feng, Z.; Zou, Q.; Xu, B.; Wang, Y.; Gao, H.; Yin, C.; Li, R.; Wang, J.; Huang, W., Side-Chain Functionalized Polymer Hole-Transporting Materials with Defect Passivation Effect for Highly Efficient Inverted Quasi-2D Perovskite Solar Cells. *Adv. Funct. Mater.* **2023**, *n/a* (n/a), 2304881.
- Wu, J.; Liu, C.; Li, B.; Gu, F.; Zhang, L.; Hu, M.; Deng, X.; Qiao, Y.; Mao, Y.; Tan, W.; Tian, Y.; Xu, B., Side-Chain Polymers as Dopant-Free Hole-Transporting Materials for Perovskite Solar Cells—The Impact of Substituents' Positions in Carbazole on Device Performance. ACS Appl. Mater. Interfaces 2019, 11 (30), 26928-26937.
- 252 Huang, C.; Potscavage, W. J.; Tiwari, S. P.; Sutcu, S.; Barlow, S.; Kippelen, B.; Marder, S. R., Polynorbornenes with pendant perylene diimides for organic electronic applications. *Polym. Chem.* **2012**, *3* (10).
- Hüttner, S.; Sommer, M.; Thelakkat, M., n-type organic field effect transistors from perylene bisimide block copolymers and homopolymers. *Appl. Phys. Lett.* 2008, 92 (9), 093302.
- Lepage, M. L.; Simhadri, C.; Liu, C.; Takaffoli, M.; Bi, L.; Crawford, B.; Milani, A. S.; Wulff, J. E., A broadly applicable cross-linker for aliphatic polymers containing C–H bonds. *Science* 2019, *366* (6467), 875-878.
- Kim, M. J.; Lee, M.; Min, H.; Kim, S.; Yang, J.; Kweon, H.; Lee, W.; Kim, D. H.; Choi, J. H.; Ryu, D. Y.; Kang, M. S.; Kim, B.; Cho, J. H., Universal threedimensional crosslinker for all-photopatterned electronics. *Nat. Commun.* 2020, *11* (1), 1520.
- 256 Zhu, Z.; Chueh, C.-C.; Zhang, G.; Huang, F.; Yan, H.; Jen, A. K. Y., Improved Ambient-Stable Perovskite Solar Cells Enabled by a Hybrid Polymeric Electron-Transporting Layer. *ChemSusChem* **2016**, *9* (18), 2586-2591.
- 257 Zheng, Y.-Q.; Lei, T.; Dou, J.-H.; Xia, X.; Wang, J.-Y.; Liu, C.-J.; Pei, J., Strong Electron-Deficient Polymers Lead to High Electron Mobility in Air and Their Morphology-Dependent Transport Behaviors. *Adv. Mater.* **2016**, *28* (33), 7213-7219.
- Yang, C.-Y.; Stoeckel, M.-A.; Ruoko, T.-P.; Wu, H.-Y.; Liu, X.; Kolhe, N. B.; Wu, Z.; Puttisong, Y.; Musumeci, C.; Massetti, M.; Sun, H.; Xu, K.; Tu, D.; Chen, W. M.; Woo, H. Y.; Fahlman, M.; Jenekhe, S. A.; Berggren, M.; Fabiano, S., A high-

conductivity n-type polymeric ink for printed electronics. *Nat. Commun.* **2021**, *12* (1), 2354.

- 259 Sharma, A.; Singh, S.; Song, X.; Rosas Villalva, D.; Troughton, J.; Corzo, D.; Toppare, L.; Gunbas, G.; Schroeder, B. C.; Baran, D., A Nonionic Alcohol Soluble Polymer Cathode Interlayer Enables Efficient Organic and Perovskite Solar Cells. *Chem. Mater.* 2021, *33* (22), 8602-8611.
- 260 Liu, Y.; Sheri, M.; Cole, M. D.; Emrick, T.; Russell, T. P., Combining Fullerenes and Zwitterions in Non-Conjugated Polymer Interlayers to Raise Solar Cell Efficiency. *Angew. Chem. Int. Ed.* **2018**, *57* (31), 9675-9678.
- 261 Yang, R.; Tian, J.; Liu, W.; Wang, Y.; Chen, Z.; Russell, T. P.; Liu, Y., Nonconjugated Self-Doped Polymer Zwitterions as Efficient Interlayers for High Performance Organic Solar Cells. *Chem. Mater.* **2022**, *34* (16), 7293-7301.
- Liu, M.; Fan, P.; Hu, Q.; Russell, T. P.; Liu, Y., Naphthalene-Diimide-Based Ionenes as Universal Interlayers for Efficient Organic Solar Cells. *Angew. Chem. Int. Ed.* 2020, 59 (41), 18131-18135.
- Liu, J.; Deng, Y.; He, X.; Liu, G.; Li, X., 2,2,2-Trifluoroethanol-Assisted Construction of 2D/3D Perovskite Heterostructures for Efficient and Stable Perovskite Solar Cells Made in Ambient Air. ACS Appl. Mater. Interfaces 2023, 15 (28), 33550-33559.
- Lian, J.; Lu, B.; Niu, F.; Zeng, P.; Zhan, X., Electron-Transport Materials in Perovskite Solar Cells. *Small Methods* **2018**, *2* (10).
- 265 Momblona, C.; Gil-Escrig, L.; Bandiello, E.; Hutter, E. M.; Sessolo, M.; Lederer, K.; Blochwitz-Nimoth, J.; Bolink, H. J., Efficient vacuum deposited p-i-n and n-i-p perovskite solar cells employing doped charge transport layers. *Energy Environ. Sci.* 2016, 9 (11), 3456-3463.
- 266 Jung, S. K.; Lee, D. S.; Ann, M. H.; Im, S. H.; Kim, J. H.; Kwon, O. P., Non-Fullerene Organic Electron-Transporting Materials for Perovskite Solar Cells. *ChemSusChem* 2018, 11 (22), 3882-3892.
- 267 Jung, S. K.; Heo, J. H.; Lee, D. W.; Lee, S. H.; Lee, S. C.; Yoon, W.; Yun, H.; Kim, D.; Kim, J. H.; Im, S. H.; Kwon, O. P., Homochiral Asymmetric-Shaped Electron-Transporting Materials for Efficient Non-Fullerene Perovskite Solar Cells. *ChemSusChem* 2019, *12* (1), 224-230.
- 268 Nakayama, K.-i.; Hashimoto, Y.; Sasabe, H.; Pu, Y.-J.; Yokoyama, M.; Kido, J., Electron Injection and Transport Properties of Phenazine Compounds with Fused Rings. Jpn. J. Appl. Phys. 2010, 49 (1), 01AB11.
- Guo, J.; Zheng, C.-J.; Ke, K.; Zhang, M.; Yang, H.-Y.; Zhao, J.-W.; He, Z.-Y.; Lin, H.; Tao, S.-L.; Zhang, X.-H., Novel triazine derivatives with deep LUMO energy levels as the electron-accepting components of exciplexes. *J. Mat. Chem. C* 2021, 9 (3), 939-946.
- Oliver, R. D. J.; Caprioglio, P.; Peña-Camargo, F.; Buizza, L. R. V.; Zu, F.; Ramadan, A. J.; Motti, S. G.; Mahesh, S.; McCarthy, M. M.; Warby, J. H.; Lin, Y.-H.; Koch, N.; Albrecht, S.; Herz, L. M.; Johnston, M. B.; Neher, D.; Stolterfoht, M.; Snaith, H. J., Understanding and suppressing non-radiative losses in methylammonium-free wide-bandgap perovskite solar cells. *Energy Environ. Sci.* 2022, *15* (2), 714-726.

- 271 Lin, R.; Xu, J.; Wei, M.; Wang, Y.; Qin, Z.; Liu, Z.; Wu, J.; Xiao, K.; Chen, B.; Park, S. M.; Chen, G.; Atapattu, H. R.; Graham, K. R.; Xu, J.; Zhu, J.; Li, L.; Zhang, C.; Sargent, E. H.; Tan, H., All-perovskite tandem solar cells with improved grain surface passivation. *Nature* **2022**, *603* (7899), 73-78.
- Palmstrom, A. F.; Eperon, G. E.; Leijtens, T.; Prasanna, R.; Habisreutinger, S. N.; Nemeth, W.; Gaulding, E. A.; Dunfield, S. P.; Reese, M.; Nanayakkara, S.; Moot, T.; Werner, J.; Liu, J.; To, B.; Christensen, S. T.; McGehee, M. D.; van Hest, M. F. A. M.; Luther, J. M.; Berry, J. J.; Moore, D. T., Enabling Flexible All-Perovskite Tandem Solar Cells. *Joule* 2019, *3* (9), 2193-2204.
- Zhao, D.; Chen, C.; Wang, C.; Junda, M. M.; Song, Z.; Grice, C. R.; Yu, Y.; Li, C.;
 Subedi, B.; Podraza, N. J.; Zhao, X.; Fang, G.; Xiong, R.-G.; Zhu, K.; Yan, Y.,
 Efficient two-terminal all-perovskite tandem solar cells enabled by high-quality lowbandgap absorber layers. *Nat. Energy* 2018, *3* (12), 1093-1100.
- Huang, D.; Guo, C.; Li, Z.; Zhou, H.; Zhao, X.; Feng, Z.; Zhang, R.; Liu, M.; Liang, J.; Zhao, L.; Meng, J., Machine learning-assisted screening of effective passivation materials for P–I–N type perovskite solar cells. *J. Mat. Chem. C* 2023, *11* (28), 9602-9610.
- 275 Zhi, C.; Wang, S.; Sun, S.; Li, C.; Li, Z.; Wan, Z.; Wang, H.; Li, Z.; Liu, Z., Machine-Learning-Assisted Screening of Interface Passivation Materials for Perovskite Solar Cells. ACS Energy Lett. 2023, 8 (3), 1424-1433.
- 276 Liu, W.; Lu, Y.; Wei, D.; Huo, X.; Huang, X.; Li, Y.; Meng, J.; Zhao, S.; Qiao, B.; Liang, Z.; Xu, Z.; Song, D., Screening interface passivation materials intelligently through machine learning for highly efficient perovskite solar cells. *J. Mat. Chem. A* 2022, 10 (34), 17782-17789.
- 277 Kim, J.; Hwang, T.; Lee, B.; Lee, S.; Park, K.; Park, H. H.; Park, B., An Aromatic Diamine Molecule as the A-Site Solute for Highly Durable and Efficient Perovskite Solar Cells. *Small Methods* **2019**, *3* (1), 1800361.
- 278 The interface is still the device. *Nat. Mater.* **2012**, *11* (2), 91-91.