Synthesis of metal halide perovskites for photoredox catalysis, photoelectgric devices, and solid-state characterization of main group materials

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**ENVIRONMENTALLY BENIGN AND ENERGY EFFICIENT
SYNTHESIS OF METAL HALIDE PEROVSKITES FOR
PHOTOREDOX CATALYSIS, PHOTOELECTRIC DEVICES,
AND SOLID-STATE CHARACTERIZATION OF MAIN GROUP
MATERIALS**

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ZONGHAN HONG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological University in partial
fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

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Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals where I was the first author.

Chapter I is published as Z. Hong, W. K. Chong, A. Y. R. Ng, M. Li, R. Ganguly, T. C. Sum and H. S. Soo. Hydrophobic Metal Halide Perovskites for Visible-Light Photoredox C-C Bond Cleavage and Dehydrogenation Catalysis. *Angew. Chem. Int. Ed.*, (2019). DOI: 10.1002/anie.201812225.

The contributions of the co-authors are as follows:

- Dr. Soo provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was also revised by Prof. Sum and Dr. Li.
- I co-designed the study with Dr. Soo and performed all the laboratory work. I also analyzed the data. All VT-PL experiments was conducted by W. K. Chong.
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The contributions of the co-authors are as follows:

- Prof. Chiba and Dr. Soo conceived the research project.
- The manuscript was revised together with D. Y. R. Ong, Dr. Nishiyama, Dr. Soo, Prof. Hirao and Prof. Chiba.
- I performed the material characterizations and data analysis of PXRD, XPS, TEM. I conducted the Rietveld analysis of the powder X-ray diffraction data.
- D. Y. R. Ong performed the data collection and analysis of ssNMR.
- Prof. Hirao conducted the DFT studies.

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Table of contents

ACKNOWLEDGEMENT

TABLE OF CONTENTS I

ABSTRACT V

LIST OF ABBREVIATIONS..... VII

PREFACE..... 1

Artificial photosynthesis.....1

Metal halide perovskite – a new candidate in photocatalysis5

Mechanochemistry for perovskites9

Main group materials for environmental benign applications11

CHAPTER I

ROAD TO HYDROPHOBIC METAL HALIDE PEROVSKITES FOR VISIBLE-LIGHT DRIVEN,
PHOTOREDOX CATALYSIS

1.1 Introduction17

1.2 Synthetic of the materials.....18

1.3 Results and Discussion

1.3.1 THF as a solvent 20

1.3.2 Intercalation method 21

1.3.3 (FBA) ₂ MI ₄ perovskite	23
1.3.4 (HDA) ₂ MI ₄ perovskites	34
1.4 Photoredox catalysis	45
1.5 Conclusions	50
1.6 Crystallographic data	52
1.7 Materials and instrumental details	
Materials	58
Instrumental details	59
Details of substrates syntheses and photocatalytic studies	60
Photocatalytic studies	61
NMR data for the substrates in photocatalytic studies:	62

CHAPTER II

SOLVENT-FREE, KILOGRAM-SCALE, MECHANOCHEMICAL SYNTHESIS OF PHASE-PURE, METASTABLE METAL HALIDE PEROVSKITES

2.1 Introduction	67
2.2 Results and discussion	
2.2.1 Solvent-free, mg- to kg-scale syntheses of phase-pure perovskites	68
2.2.2 Solvent-free fabrication of functional devices	78
2.3 Conclusions	81
2.4 Materials, instrumental details and synthetic methods	82
Mechanochemical syntheses	84
2.5 Supplementary characterization data	89

CHAPTER III

UNDERSTANDING THE ORIGINS OF NUCLEOPHILIC HYDRIDE REACTIVITY OF SODIUM

HYDRIDE-IODIDE COMPOSITE

3.1 Introduction	104
3.2 Materials Characterization of NaH-LiI and NaH-NaI Composites.....	106
3.3 Conclusions	119
3.4 Experimental section	
Sample preparation of NaH-NaI and NaH-LiI composites.....	120
Experimental Details for PXRD.....	121
X-ray photoelectron spectroscopy (XPS) experiments	122
Solid-state NMR measurements	129
SUMMARY AND OUTLOOK.....	131
REFERENCES.....	135
LIST OF PUBLICATIONS.....	153

Abstract

Extensive research has been carried out to address the rising concerns of high energy consuming industry and environmental problems. In this thesis, three main projects have been developed and thoroughly investigated, dedicated to addressing some of these problems. The first two chapters focus on the syntheses and applications of metal halide perovskites while the third chapter reveals a different perspective of main group chemistry regarding NaH-NaI composite that promotes dehalogenation and decyanation to mitigate the environmental impact of harmful organic compounds. As earth-abundant materials, metal halide perovskites have been attracting broad research interest as photosensitizers with promising photoelectric and photophysical properties but their application in photocatalysis is severely under-explored. Meanwhile, the scalability and reproducibility of the synthesis are still below satisfactory. Targeting these issues, energy efficient syntheses of metal halide perovskites were developed up to kg-scale, and the products were successfully employed in artificial photosynthesis and the fabrication of photoelectrical devices. Additionally, a characterization study of simple NaH-NaI composite that performs dehalogenation and decyanation was conducted, revealing a thorough understanding of the unique reactivity and an alternative approach to reduce the adverse environmental impacts caused by hazardous industry chemicals.

List of abbreviations

DSSC	dye-sensitized solar cell
PCE	power conversion efficiency
LED	light-emitting diode
SET	single electron transfer
MLCT	metal to ligand charge transfer
NHE	normal hydrogen electrode
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
VB	valence band
VBM	valence band maximum
CB	conduction band
MA	methyllummonium
FA	formamidinium
HDA	1-hexadecylammonium
FBA	4-fluorobenzylammonium
HI	hydroiodic acid
NBS	<i>N</i> -bromosuccinimide
Me	methyl group
Cat.	catalyst
Cp*	pentamethylcyclopentadienyl
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
THF	tetrahydrofuran

DCM	dichloromethane
DE	diethyl ether
ACN	acetonitrile
CA	contact angle
PXRD	powder X-ray diffraction
UV-vis DRS	ultraviolet-visible diffuse reflectance spectroscopy
FTIR	Fourier transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy
CV	cyclic voltammetry
PL	photoluminescence
TRPL	time-resolved photoluminescence
VTPL	variable-temperature photoluminescence
SEM	scanning electron microscopy
TEM	transmittance electron microscopy
NMR	nuclear magnetic resonance
MS	mass spectroscopy
ppm	parts per million
DFT	density functional theory
LAG	liquid assisted grinding

Preface

In the 18th century, the Industrial Revolution lit up the light for a modern world but led to the over-exploitation of natural resources and severe environmental pollution due to the severe impact of human activities. As the third industrial revolution unfolds and flourishes, the modernization of the human society has resulted in even higher energy consumption (+2.2% growth in 2017),¹ despite the fact that the global population growth has steadily slowed down in the last decade. Meanwhile, the history continues to unfold in a very similar way: huge amounts of daily exhausts are being released as pollutants to the atmosphere, tremendous amounts of solid wastes containing toxic materials are being dumped and buried in soil, trillions of liters of liquid wastes charged with hazardous chemicals are being disposed into rivers and oceans. These human practices are believed to lead our society to an ordeal situation with the suffer from resource depletion and lack of living habitat, which have led to the steady extinction of many species. Just like what Dr. Jared Diamond tried to reiterate, we have come to a point to make another choice.²

Artificial photosynthesis

Upon being released to the atmosphere, carbon-based exhausts have been substantially interfering with the natural climate regulation. The control of exhausts and the recycling of carbon has become an inevitable issue to resolve for the mankind. However, fossil fuels remain as the major energy resource for most well-established industries including power plants, automobiles, and manufacturing facilities. Regardless of the massive energy consumption of our society, we are never short of renewable energy sources on this planet. Compared to other fossil fuel sources, several energy technologies have been successfully designed and developed ready to contribute though subject to various limitations. Among

all the renewable energy sources, solar energy is believed to be one of the most ideal sources of energy on Earth since it is highly abundant and clean. We are receiving over 3 million EJ solar energy whereas the total energy used is approximately 600 EJ each year.³ Meanwhile, over 42% of sunlight is in the visible-light region which reveals the importance of utilization of visible-light.⁴ With hope to catch up with the energy consumption of the whole world, researchers are sparing no efforts to develop the technologies for renewable energy. CSP-stirling (commercial concentrating solar thermal power with dish Stirling engine) technology for example, has the highest efficiency as 30% compared to other solar energy harvesting technologies.⁵

However, solar power is still highly underutilized despite of the fact that solar panel technology is constantly improving and has been well commercialized.¹ Singapore, for instance, receives over 100 times as much energy as we use from solar energy, of which at least 10% can be realistically harnessed with current photovoltaic technology. Another drawback of the solar panel is the lack of efficient approach for the storage and transit of power with the concern of uneven distribution of sun light on this planet. The photosynthesis comes in as a perfect compensation because most of the final products can be stored and transported with relative ease. Photosynthesis is one of the main natural processes for converting solar energy to usable energy sources, facilitating the carbon recycling in the atmosphere.⁶ By mimicking the natural process, artificial photosynthetic system has been proposed as a promising solution for the existing pollution and energy issues.

There has been a rapid increase in the publication of research related to artificial photosynthesis.⁷ In general, artificial photosynthesis can be a CO₂-emission free, non-polluting approach to transform the endless solar energy into more usable energy sources such as solar fuels and high-value raw materials. By the implementation of reduction

reaction driven by sunlight, CO₂ can be utilized as the main carbon source being reduced and transformed to other molecules in forms of chemical fuels, therefore the recycle of released CO₂ can be established. The equilibrium of atmospheric constitution can be rebalanced for the natural climate regulation. Moreover, artificial photosynthesis can also be used to store solar energy in safe, clean and renewable forms such as biomass and stable chemicals. These stored energy can be directly utilized for multiple purposes. Meanwhile, these chemicals present relatively simple chemical constituents which makes them much cleaner and more efficient than conventional combustible fuels.

Scheme 1. Illustration of the concept of artificial photosynthesis.

The main concept of hybrid artificial photosynthetic system has been established based on the development of semiconductors and biomimetic complexes.⁸ In a typical one, dye molecules or semiconductors will be the visible-light photosensitizers powering the photo-redox reactions. These light harvesters will perform charge separation generating different charge carriers. With the excited electrons supplied by photosensitizers, CO₂ and proton can be reduced by metal complex molecular catalysts to give usable chemical fuels such as methanol and hydrogen gas respectively. On the other side, chemical pollutants or biomass will be oxidized by the positive charges and degraded to more useful small

molecules. In this process, metal-complex co-catalysts are anchored to the photosensitizers as the active centers of the chemical reactions.⁹

The components of the system should have a proper alignment of energy levels to guarantee the efficient charge extraction. The photosensitizers are the essential parts of these systems. As the driving force of the system, the semiconductor harvests photons of energies within the visible region of the solar spectrum, providing excited electrons for the reduction reaction, while also offering vacancies for electrons coming from the oxidation side. Thus, the criteria of photosensitizers are: 1) panchromatic absorption, wide absorption range within visible-light region is essential for a visible-light photosensitizer; 2) slow recombination rate, which guarantees the efficiency charge extraction. The lifetime of excited states should be long enough for molecular catalysts to carry out the reactions; 3) suitable band gap and energy level, which is crucial for the functioning of the system. There are also other criteria of good photosensitizers such as non-toxicity, ambient stability, cost and ease of fabrication. The morphology and size of these materials can also play important roles to improve their performance in the system.¹⁰⁻¹²

As the major component of the system, photoredox catalysis has recently been established as a versatile methodology in the synthetic toolkit of organic chemists through a series of seminal studies by MacMillan,¹³⁻¹⁶ Yoon,^{17,18} Stephenson, and Fukuzumi,^{19,20} which have demonstrated its general applicability under mild reaction conditions. Nonetheless, the molecular photosensitizers employed in most photoredox reactions have predominantly been Ru- or Ir-based dyes that harvest radiation from the blue-end of the optical spectrum, due to their combination of effective photoexcited state lifetimes and suitable redox potentials for mediating the desired chemistry. A particular challenge has been the discovery of heterogeneous photosensitizers that can span the visible spectrum and

possesses the appropriate redox properties to mediate the desired single electron transfer (SET) processes in photoredox reactions.²¹⁻²³

Metal halide perovskite – a new candidate in photocatalysis

Hybrid lead halide perovskites have received overwhelming attention over the past decade due to their exceptional performance as optoelectronic materials. Specifically, the methylammonium (MA), formadinium (FA), and cesium lead iodide (CsPbX₃) perovskites have been incorporated into solar cells that have achieved solar energy conversion efficiencies in excess of 22%.²⁴⁻³¹ Furthermore, MAMX₃, FAMX₃, CsMX₃ (M = Pb, Sn; X = I, Br, Cl), and their ion permutations have found applications in light-emitting diodes,³²⁻³⁵ non-linear absorption,³⁶⁻³⁸ and lasers.³⁹⁻⁴¹ When it comes to the synthesis of integrated nanomaterials, the solution-processability makes these materials much more feasible to fabricate and be loaded into the porous structure. Moreover, the tunable organic part of perovskites makes it possible to form a direct bonding with co-catalysts, which can lead to a better performance of charge extraction. Therefore, by loading perovskites into mesoporous metal oxide semiconductors, a new type of integrated nanomaterial with enhanced light harvesting ability will be obtained and then applied in the artificial photosynthetic system. Meanwhile, upon the achievement of improved stability, it is also aimed to assess their potential capability as photocatalysts in a heterogeneous catalytic system.

Perovskite type materials were first described in 1839 as a calcium titanium oxide mineral and was named after the Russian mineralogist Lev Perovski. Compounds that have

a similar crystal structure as CaTiO_3 are classified as perovskites. By replacing small cations with organic methylammonium groups, the inorganic-organic hybrid perovskite was first employed as a novel hole-transfer material (HTM) in solid-state dye sensitized solar cells (ssDSSCs) due to its high charge carrier mobility,^{42,43} followed by a flourish of research exploring their ideal light-harvesting abilities as photosensitizers.^{44,45,46} Perovskites has since become some of the most studied materials and tremendous effort and research have been devoted to the development of this revolutionary candidate for the next generation of solar cells while the perovskite based solar cells were proven to perform with over 22% efficiency.^{29,47}

For a context, DSSCs have been proposed to be superior design owing to their relatively low-cost and the ease of production.^{48,49} In DSSCs, the TiO_2 cathode is sensitized by a visible light absorbing dye to give a photocurrent. A redox shuttle can regenerate the ground state of the dye and produce a potential. However, the instability of liquid electrolytes in DSSCs limits their commercialization, resulting in the proposal of solid state DSSCs (ssDSSC) as more viable alternatives. The mechanism of function in these two solar cells are practically similar except for the replacement of the liquid electrolyte with solid hole transfer materials (HTM) in the ssDSSCs.⁴⁸ While the traditional polymer HTMs have shown low efficiency when introduced in ssDSSCs, the solution-processible perovskites have recently garnered a lot of attention as a surprisingly good alternative.⁵⁰ Recently, perovskite-based ssDSSCs have been effectively utilized for water splitting and hydrogen evolution.^{51,52} For instance, according to the work by Luo et al, the maximum power of perovskite tandem solar cells have been determined to be able to reach 9.61 mA cm^{-2} at 1.63 V, and 15% efficiency of hydrogen generation can be achieved with an optimized fabrication. These works reveal a promising perspective of a wide application and commercialization of perovskite-based ssDSSCs, which are cheaper and easier to fabricate.

Nonetheless, the current state-of-the-art perovskites have severe stability problems. For instance, some widely acknowledged shortcomings of the most popular MAPbI₃, FAPbI₃, and CsPbI₃ perovskites are their susceptibility to degradation under moist conditions and phase instability,⁵³⁻⁵⁵ which has largely precluded their use in chemical reactions where solvents are involved. For one, the perovskites containing organic ammonium cations MA and even FA are notoriously vulnerable to thermal⁵⁶⁻⁵⁸ and moisture^{54,55} degradation, and decompose due to the irreversible structural change when in contact with water,^{44,59} whereas the all-inorganic CsPbI₃ suffers from poor phase stability. The chemical process was well studied by Niu G.D. et al.⁶⁰ Only the bulk single crystal was found fairly stable in air up to 6 months, according to latest work by Dong Q. et al.⁶¹ A number of recognized decomposition pathways include the deprotonation or leaching of the MA and FA cations, the unusually high iodide conductivity, and the inhomogeneous grain characteristics of perovskite layers, all of which transform the perovskites into metastable materials.⁶² In addition, the morphology control and nanoscale properties are still under explored though the synthesis is relatively straightforward.^{10,63-69}

In the case of artificial photosynthesis, the stability of the material under ambient conditions and in protic solvents is a crucial criterion. The ideal working conditions for artificial photosynthesis include AM 1.5 solar irradiation, room temperature, standard atmospheric pressure and aqueous media. Our photosensitizers should be functioning under these conditions in either a homogeneous system or a heterogeneous system. However, as mentioned earlier, typical MA/FA based 3D perovskites are prone to react with water and conceive irreversible structural changes due to the hygroscopic nature of these organic cations. It is proposed that the water-sensitivity can be reduced by changing the simple methylammonium cation with bulky or non-polar organic groups to reduce the interference from water molecules.⁷⁰ Thus the stability of the perovskite structure can be enhanced in

protic or aqueous media.⁷¹ It has also been reported that certain large cations can be added as additives to increase the stability and the quality of thin films due to their adjacent function on the surface.⁷² The mixed halide perovskites are also intensively researched due to their better stabilities compared to the pure triiodide congener.⁴⁴ Substituting MA with other cationic components, like FA or Cs⁺, will also facilitate better thermodynamic stability of perovskites although the photoelectric and photophysical properties vary in specific cases.^{27,62,73} Regarding the influence of this cation change on the photophysical properties, it is revealed that 2D perovskites normally demonstrate relatively larger band gaps and much higher exciton binding energies. These influences are not ideal for solar cells even with a significant improvement of stability.^{71,74} Nevertheless, these alterations in photophysical properties should unlikely affect their applications in photoredox catalysis due to the intrinsic nature of charge generation upon photo-exciting.

Besides the role as dyes for charge generation, the outstanding performance in optoelectronic devices lately suggest that perovskite materials may be promising candidates for functional catalyts in photoredox chemistry. Regardless of the worldwide effort devoted in developing this type of materials for photovoltaic devices, very few studies about perovskites' photoredox ability has been published to date. The use of these perovskites in photocatalysis and artificial photosynthesis have been severely underexplored,⁷⁵⁻⁷⁷ despite their remarkable light harvesting abilities. In 2016, Park S. et al. employed tetragonal MAPbI₃ in a visible-light photocatalytic system for HI splitting which featured an efficient H₂ production.⁷⁵ The highly concentrated HI aqueous solution is critical to maintain the equilibrium between the crystallization and dissolution of MAPbI₃. This pioneering work demonstrates the great potential of perovskites to be applied as functional photosensitizers for artificial photosynthesis. Early in 2017, a composite of CsPbBr₃ perovskite quantum dots and graphene oxide (CsPbBr₃ QD/GO) was successfully applied as a catalyst for CO₂

reduction reported by Xu Y. F. et al.⁷⁶ It was found in this study that GO provides a more feasible pathway to separate the electron-hole pairs that are generated by CsPbBr₃ QDs due to the conductive nature of GO. This result again strongly indicated that the potential charge separation and electron transfer, which is essential for photoredox catalysis, can be achieved with perovskites.

Herein, this thesis intends to discuss the possible capabilities of perovskite materials in our system as an enhancement to the photosensitizers. Lead-free perovskites were also synthesized and studied as possible alternatives with reduced toxicity and better visible-light harvesting ability. The processability and scalability of the synthesis of metal halide perovskites will also be discussed and a new approach of fabricating photoelectrical devices will be proposed as a complete solvent free method.

Mechanochemistry for perovskites

For the state-of-the-art perovskite materials, the phase purity and crystallinity of the products are found to be sensitive to the solvents used and the synthetic procedures. For instance, the syntheses often involve dissolving the precursors in hazardous solvents such as *N,N*-dimethylformamide (DMF) followed by either spin-coating, spray-coating, or drop-casting the solutions onto substrates, resulting in thin perovskite films. In many cases, these films are further processed by annealing at elevated temperatures, enabling polymorphic transformation to form the desired perovskite phases. Such solution-based processes add further complications to their widespread utilization since the reproducibility and scalability of these methods beyond small devices remain unsubstantiated.

Recently, alternative synthetic methodologies such as mechanochemistry have proven to efficiently and reproducibly provide access to metastable products in solvent-free

environments, where traditional solution-based chemistry proved unsuccessful.^{78,79} Modern mechanochemical reactions are performed using automated ball mills, such as shaker mills or large-scale planetary mills. In these mills, the reaction vessel (or jar) is charged with ball bearings, typically made of hardened stainless steel, and is oscillated or spun at a controlled speed. Such solid-state milling methods circumvent the need to find suitable solvents and have enabled access to compounds that were previously unattainable using solution-based methodologies.⁸⁰ Although mechanochemistry had predominantly been employed in the preparations of pharmaceutical cocrystals and inorganic alloys and oxides,⁷⁸ sporadic efforts by several groups have demonstrated its compatibility for the synthesis of a small number of air-stable lead halide perovskites.⁸¹⁻⁸⁵ Although these examples have focused on room temperature stable lead-based perovskites, we envisioned that the replacement of the toxic lead and the organic cations will be vital for the future sustainability of perovskite devices. Moreover, in these few previous reports, although the perovskite synthesis was conducted in small scales without solvents, the subsequent device fabrication involved solution processing, which could result in chemical transformation of the desired metastable perovskite into other phases.

Herein, a unique solvent-free preparation of crystalline, phase-pure, all-inorganic CsSnX_3 ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) perovskites by ball milling readily available cesium and tin(II) halide salts was developed. FAPbI_3 and CsPbI_3 perovskites in their high-temperature stable phases were also prepared at room temperature to emphasize the generality of our approach. The products are isolated as homogeneous powders without the need for additional thermal annealing or further purification. The perovskites have been systematically characterized and show reproducible, enhanced phase purity relative to the usual solution-based methods. In addition, the mechanochemical reaction is readily scalable (Figure 2.1) and the desired perovskite products can be obtained from mg up to kg scales, by using a vibrational shaker

mill and a planetary mill respectively. Notably, we demonstrate that the powdered products can be easily converted into pellets under pressure and perform as effective photodetectors. Metal halide perovskites have been proposed to be promising candidates for photodetectors compared to traditional inorganic semiconductors, which are synthesized under much harsher conditions with poor scalabilities. This report illustrates how we used unconventional energy inputs to not only synthesize perovskites, but also fabricate functional, sustainable energy, perovskite devices in practical scales under virtually solvent-free conditions.

Main group materials for environmental benign applications

Regarding the concern about toxic anions such as halide and cyanide that are widely present as function groups in industrial chemicals including pesticides, refrigerants and solvents, the detoxication of these compounds has become an intriguing yet pressing topic in the academic society. Dehalogenation reactions have been intensively studied following the wide usage of these halogenated compounds. In 2015, Bhattacharjya A. et al. reported dehalogenation of aryl compounds under mild conditions (room temperature or 50 °C in water) using palladium as a catalyst. This system appeared to be an attractive approach due to the avoided ligand synthesis and the use of aqueous reaction media, which also benefits the recyclability of the catalyst.⁸⁶ Earlier in 2007, main group compounds indium(III) acetate and gallium trichloride were effectively applied as catalysts for the reduction of haloalkanes under mild conditions.⁸⁷ It was recently found out that reductive dehalogenation is able to occur without using noble metals as catalysts. Ueno R. et al. reported a radical based reduction of aryl halides in 2016 using cesium carbonate as a base and 2-propanol as a reductant. This radical reaction was initiated by a radical initiator de-tert-butyl peroxide while the yields were generally good, although prolonged heating was required.⁸⁸

Meanwhile, decyanation has also been one of the key research field encouraged by the concept of more environmental benign industry. Tobisu M. et al. reported a selective cleavage carbon-cyano bonds in a wide scope of nitriles using a rhodium complex as catalyst.⁸⁹ It is self-evident that main group materials and compounds are getting more favored in the context of green chemistry, regardless that transition metals are still dominating the field of catalysis.

Besides the compounds being explored in organic synthesis and metal halide perovskites, main group materials comprise of a much wider scope of candidates such as GaAs, GaN,⁹⁰ and graphitic carbon nitride, some of which have been successfully applied for photocatalysis.^{91,92} Certain essential consumer products based on main group materials have been developed and vigorously pursued to change the way we live due to their energy applications, lithium-ion battery for instance. Materials like carbon nanotubes have drawn broad attention considering their high values in future applications. Another example is ammonia borane, which is highly sought after as a promising material for hydrogen storage and transport media.⁹³ More generally, in the realm of synthetic chemistry, main group compounds like organolithium and Grignard reagents are widely accepted as stoichiometric reagents for essential reactions.

Among all these main group materials, hydride compounds are commonly used for various applications, from CaH_2 as a typical desiccant to palladium hydride being charged in hydrogen fuel-cell automobiles. Mostly, hydrides are treated as strong bases and reducing agents in synthesis, such as NaH and NaBH_4 respectively. Sodium hydride (NaH) is one of the simplest earth-alkaline metal ionic hydride compounds. The property was believed exclusively to be Brønsted basic while single electron transfer (SET) activity was found in most reaction schemes.⁹⁴⁻⁹⁶ The hydride (H^-) transfer behavior of NaH has scarcely been

studied.⁹⁷⁻¹⁰² However, it was recently discovered that NaH was able to facilitate reductive decyanation reaction via hydride transfer when sodium iodide (NaI) or lithium iodide (LiI) were present as additives.¹⁰³⁻¹⁰⁶ In addition, magnesium iodide (MgI₂) was found to be suitable for this unprecedented reaction as well, which indicated the important role of iodide species in these systems.¹⁰³ Therefore in this thesis, the third chapter is devoted to discuss the origin of this unique reactivity by a thorough solid-state characterization of NaH-NaI composite.

Chapter I

Road to hydrophobic metal halide perovskites for visible-light driven, photoredox catalysis

This chapter comprises of a work that has been submitted for publication. The authors include Zonghan Hong, Wee Kiang Chong, Andrew Yun Ru Ng, Mingjie Li, Rakesh Ganguly, Tze Chien Sum, Han Sen Soo. The author of this thesis contributed in the major part of this work. H.S.S., Z.H. conceived the research. Z.H. designed the experiments and performed the synthetic, characterization and photocatalysis experiments. W.K.C collected the VTPL and VT-TRPL data and analyzed the results.

ABSTRACT: The academic attention to organic-inorganic metal halide perovskites has skyrocketed and continued to maintain at a very high extent up to date. While numerous engineering approaches have been attempted to improve the stability of perovskite devices, we intend to chemically address the stability issue by altering the organic component in the crystal lattice to introduce desired chemical property. The studies on FBA and HDA as building blocks for perovskites will be discussed in this chapter and the importance of a feasible synthesis that has been developed is highlighted as well. By intercalating the long alkyl group 1-hexadecylammonium (HDA) between the inorganic layers, two-dimensional lead and tin halide perovskites were successfully synthesized. It was observed to have

visible light absorption and narrow-band photoluminescence. Due to their inherent hydrophobicity and stability even in humid atmospheric conditions, we applied these perovskites in the decarboxylation and dehydrogenation of indoline acids with $(\text{HDA})_2\text{PbI}_4$ or $(\text{HDA})_2\text{SnI}_4$ as photoredox catalysts, with quantitative conversions and high yields for the former. This original application of the organic-inorganic metal halide perovskites is highlighted in this chapter.

1.1 Introduction

Hybrid lead halide perovskites have received overwhelming attention over the past decade due to their exceptional performance as optoelectronic materials. However, the use of these perovskites in photocatalysis and artificial photosynthesis have been limited,⁷⁵⁻⁷⁷ despite their remarkable light harvesting abilities. It is hypothesized that perovskite materials can be applied as photocatalysts for photoredox reactions, given improved stability in organic media for suitable organic reactions.

In this context, this project sought hydrolytically stable, two-dimensional (2D) perovskites with well-defined crystalline morphology to circumvent their documented degradation deficiencies and create more robust materials suitable for driving photoredox reactions in organic solvents. In this chapter, the synthesis and fundamental characterization of several new hybrid perovskites with improved stability are discussed. A new simple synthetic approach that was successfully developed using tetrahydrofuran (THF) as a solvent will be discussed. Various characterizations have been performed including Uv-vis spectroscopy, powder X-ray diffraction study, single-crystal X-ray diffraction study, transmission electron microscopy, photoluminescence spectroscopy, X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, Fourier-transformed infrared spectroscopy, time correlated single photon counting, nuclear magnetic resonance spectroscopy and elemental analysis. Lead free perovskites were also synthesized and studied to be possible alternatives with relatively less toxicity. The hydrophobic (HDA)₂ML₄ perovskites were further exploited in photoredox decarboxylations and dehydrogenations to illustrate that these perovskites are viable as visible light harvesters for photodriven organic syntheses.

1.2 Synthesis of the materials

One of the motivations was to improve the stability of metal halide perovskites in solvents, especially protic media. We anticipated that long, hydrophobic, aliphatic chains close-packed in the perovskite structure between the inorganic layers would repel water molecules. As reported recently,^{7,107} the synthesis of ammonium perovskites has been established for some specific examples, but adaptations are needed for the synthesis of other derivatives. Herein, a two-step method was developed to synthesize FBA/HDA based perovskites. The FBAI/HDAI salt was first prepared and isolated as a solid precursor. Metal halides were then mixed with FBAI or HDAI tetrahydrofuran (THF) to give the precursor solutions. The perovskite products crystallized from the precursor solutions by vapor diffusion of diethyl ether into the THF at room temperature. Although PbI_2 or SnI_2 do not dissolve well in anhydrous THF, homogeneous THF solutions of the FBA/HDA-based perovskites readily formed when the precursors were mixed at room temperature. The use of THF for the crystallization and preparation of perovskites is attractive due to the low energy cost of removing the volatile THF.

Methylammonium iodide (MAI): Methylamine (CH_3NH_2 2.4 mL, 23 mmol, 40% in methanol, TCI) was mixed with 3 mL HI (57 wt% aq. Sigma-Aldrich) and 10 mL methanol while vigorously stirred for 2 hours at 0 °C. The as-prepared solution was dried at 50 °C for 1 hour using a rotary-evaporator. The residue was dissolved in a small amount (about 0.5 mL) of ethanol to give a concentrated solution, to which ethyl acetate was added to precipitate a white solid. The crude product was dissolved in ethanol again, precipitated out with ethyl acetate for purification, and then washed with ethyl acetate three times. The product was stored in a glovebox and dried under vacuum before use.

Compound 4-Fluorobenzylammonium iodide (FBAI): Commercially available 4-fluorobenzylamine (98%, Apollo) was mixed with 1 molar equivalent of HI (57% wt aq., Strem) and methanol while vigorously stirred for 2 hours at 0 °C. The as-prepared solution was dried at 50 °C for 1 hour using a rotary-evaporator. The residue was dissolved in a small amount of ethanol to give a concentrated solution, after which diethyl ether was added to yield a white solid. The crude product was dissolved in ethanol again and diethyl ether was added for crystallization. The product was then washed with diethyl ether three times. The product was stored in a glovebox for further usage.

Compound 1-hexadecylammonium hydroiodide (HDAI): HDA (1.8 g, 7.5 mmol) was mixed with 1.1 mL of HI (57% wt. aq.,) in 20 mL methanol with vigorous stirring for 3 h at 0 °C. The solvent was then removed under vacuum using a rotary evaporator. The residue was dissolved in a minimal amount of ethanol to give a concentrated solution, after which diethyl ether was added to yield a white solid. The product was washed with diethyl ether for three times and stored in a glovebox for further usage (2.55 g, 92% yield). ¹H NMR (DMSO-*d*₆, 500 MHz): δ = 0.85 (t, *J* = 6.8 Hz, 3 H), 1.24 (bs, 26 H), 1.50 (q, *J* = 7.5 Hz, 2 H), 2.71 – 2.81 (m, 2 H), 7.58 (s, 3 H) ppm. MS (ESI+, *m/z*) calculated for C₁₆H₃₆N⁺ [M⁺] *m/z* 242.46, found 242.23. Elemental analysis calculated (%) for C₁₆H₃₆IN: C, 52.03; H, 9.82; N, 3.79, found: C, 52.23; H, 9.64; N, 3.96.

Lead based perovskites

(FBA)₂PbI₄ perovskite: The 4-fluorobenzylammonium iodide salt and 0.5 molar equivalent of lead iodide (99.99%) were mixed in 5 mL of THF, while stirring for 2 hours at room temperature to yield a clear light-yellow solution. The as-prepared solution was dried under vacuum yielding an orange-colored powder.

(HDA)₂PbI₄ perovskite: The HDAI salt (184 mg, 0.500 mmol) and PbI₂ (115 mg, 0.250 mmol) were mixed in 5.0 mL of THF with stirring for 2 h at room temperature to yield a clear, light yellow solution. The perovskite product crystallized after vapor diffusion of diethyl ether into the as-prepared solution as pale yellow, thin flakes (136 mg, 52% yield). Elemental analysis calculated (%) for C₃₂H₇₂I₄N₂Pb: C, 32.03; H, 6.06; N, 2.34, found: C, 32.22; H, 5.83; N, 2.43.

Tin based perovskites

(FBA)₂SnI₄ perovskite. The 4-fluorobenzylammonium iodide and 0.5 molar equivalent of tin iodide (99.999%) were mixed in 5 mL of THF, while stirring for 2 hours at room temperature to yield a clear orange-yellow solution. This solution was dried under vacuum yielding a dark red flaky powder.

(HDA)₂SnI₄ perovskite. In a glove box filled with N₂, the HDAI salt (184 mg, 0.500 mmol) and SnI₂ (93 mg, 0.25 mmol) were mixed in 5.0 mL of THF with stirring for 2 h at room temperature to yield a clear yellow solution. The perovskite product crystallized after vapor diffusion of diethyl ether into the as-prepared solution as dark red, thin flakes (166 mg, 60% yield). Elemental analysis calculated (%) for C₃₂H₇₂I₄N₂Sn: C, 34.59; H, 6.53; N, 2.52, found: C, 34.89; H, 6.41; N, 2.58.

1.3 Results and Discussion

1.3.1 THF as a solvent

Due to the strong coordinating ability with lead iodide, DMF, DMSO and γ -butyrolactone have been widely used as solvents for the synthesis of perovskites and up till now these

solvents remain irreplaceable.^{67,108,109} However, various problems were encountered when using these high boiling-point solvents, especially when handled inside a glovebox. These high boiling point solvents are difficult to remove without heating and very harmful for the glovebox environment. Moreover, they are so hydrophilic that the strict moisture-free requirement cannot be met. It was challenging to find another solvent with a lower boiling-point that allowed dissolution of both the lead iodide and ammonium salt simultaneously. Meanwhile, some progress has been made to steer away from those problematic solvents. Noel N. K. et al. have successfully developed a processing method using a combination of methylamine and acetonitrile.¹¹⁰

Herein, anhydrous THF is firstly discovered to be a surprisingly good solvent for the synthesis involving organic ammonium cations like FBA and long chain ammoniums. Since lead iodide itself does not dissolve well in THF, the good solubility is speculated to be due to the unique structure of OD isolated lead halide octahedral complexes. Tin based perovskites share similar solubility in THF. The perovskite framework only starts to construct while the solvent being removed. This finding is essential to the field of perovskite engineering due to the low energy cost and feasibility provided by the low boiling-point of THF. What's more, using THF as a solvent helps us develop a feasible method to synthesize high-purity perovskites in a large scale.

1.3.2 Intercalation method

To avoid using high boiling point solvents, another feasible solution is to intercalate ammonium cations into lead iodide sheets according to the intercalating strategy proposed by Shahab A. et al.¹¹¹ Interestingly, ammonium salts showed appreciable reactivity even in the solid-state.¹¹² Thus we hypothesized that it was possible to use only the solution of ammonium salts if lead iodide nanocrystals could be synthesized to have a large enough

surface area for ammonium cations to intercalate. Various lead iodide nanocrystals were synthesized but unfortunately, it was not feasible to get large amounts of uniform product for further synthesis of perovskite.

Similarly, Zhuo et. al. reported a self-template-directed synthesis of perovskite which demonstrates a similar concept.¹¹³ In their work, a Pb precursor in form of nanowires was used as the template for perovskite. Then the transformation of precursor into perovskites was carried out by introducing the ammonium cations and bromide anions. The as-synthesized perovskite revealed an interesting porous structure. Synthesis of perovskite nanoparticles was also predicted to be feasible and superior optoelectronic performance could be achieved due to the unique nanostructure.

Inspired by these works, it was hypothesized that 2D perovskites with bulky ammonium groups can also be synthesized using nanoscale Pb precursors through a similar synthetic procedure. Lead iodide nanocrystals were successfully synthesized by Soxhlet extraction and dodecylamine (DDA) quenched method. Unfortunately, the synthesis could not be scaled up to meet the requirement of further synthesis of perovskites.

Figure 1.1. TEM images of the as prepared lead iodide nanocrystals. The samples were synthesized using a Soxhlet extraction method (left) and a DDA quenched method (right).

1.3.3 (FBA)₂MI₄ perovskite

The 4-fluorobenzylammonium (FBA) group has a similar size of the cationic ammonium group as the phenylethylammonium (PEA) cation, which has been found to be suitable for a 2D perovskite structure.^{70,114} It was hypothesized that the existence of fluorine atoms in the structure might be effective to repel water molecules as the fluorinated compounds have been exclusively studied to fabricate water repelling materials. Therefore, an enhanced moisture stability was expected of FBA perovskites compared to the reported (PEA)₂(MA)₂Pb₃I₁₀ perovskite.⁷¹ The synthesis and characterization of FBA lead perovskite was conducted. The results are discussed and reported here-in. The properties of this new materials were evaluated by comparing with published peer work.

Figure 1.2. UV-vis DRS spectrum of FBA lead perovskite.

The FBA lead perovskite has the same orange-color appearance as the PEA lead perovskite. Consistently, the UV-vis DRS (Figure 1.2) showed a significant absorbance within the visible light region with an absorption band edge at around 567 nm. Based on the UV-vis DRS data, the band gap (2.06 eV) was determined using the Tauc plotting method and linear fitting of the curve shown in Figure 1.3. This smaller band gap compared to PEA lead perovskite (2.57 eV)¹¹⁵ can be explained by in-plane distortion indicated by the properties of the bridging bond between the two PbI_6^{4-} units. According to the crystallographic data, the bridging bond angles of FBA lead perovskite are 158.0° and 158.7° , which are larger than the 151.6° and 152.9° of PEA lead perovskite, whereas the bond distance of FBA lead perovskite is 3.22 Å compared to 3.16 Å of PEA lead perovskite. The loss of the in-plane structural distortion within inorganic layers led to higher energy σ -antibonding orbitals with better spatial overlap of the Pb 6s orbitals and I 5p orbitals, that resulted in an increasing of the top of the valence band.¹¹⁶ Nevertheless, the band gaps of these 2D perovskites are significantly larger than the reported MAPbI_3 perovskite with a 3D structure (1.5 eV) due to the absence of orbital interaction along the z axis. This could be an intrinsic limitation of these perovskites in terms of light absorbing abilities.

Figure 1.3. The Tauc plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ curve of FBA lead perovskite. The slope of the curve was fitted by linear equation and extrapolated. The band gap is indicated by the intersection of fitted line with the horizontal axis.

The FBA perovskite was also probed by FT-IR spectroscopy (Figure 1.4-1.5) and compared to the spectra of FBA iodide salt. The FT-IR spectra was collected to confirm the presence of the organic groups as the characteristic amine group (N-H stretch $3500\text{-}3100\text{ cm}^{-1}$) could be clearly seen in the spectrum.

The structure of FBA lead perovskite was examined by PXRD and confirmed by a single crystal XRD study. The simulated PXRD pattern was generated automatically by the software Mercury based on the single crystal XRD data. As shown in Figure 1.7, the simulated pattern matches the experimental PXRD data well, and no peak originating from the starting materials was observed. Figure 1.6 shows a typical 2D layered pattern of PbI_6^{4-} with the FBA group packed in between every two layers. No strong interactions are observed between the two fluorine atoms due to the long distance ($3.849\text{ \AA}$), which is more than twice the van der Waals radius of a fluorine atom ($1.47\text{ \AA}$)¹¹⁴.

Figure 1.4. FT-IR transmittance spectrum of FBA lead perovskite.

Figure 1.5. FT-IR transmittance spectrum of FBA salt.

Figure 1.6. The 2D structure of FBA lead perovskite (left) and the in-phase distortion of the PbI_6^{4-} adjoining units (right) characterized by single crystal XRD. Dark grey, purple and green colors refer to lead, iodine and fluorine atoms respectively.

Figure 1.7. Powder XRD pattern of the FBA lead perovskite (black). The simulated pattern was calculated from the single crystal XRD data.

Photoluminescence of the FBA lead perovskite was investigated by fluorescence spectroscopy at room temperature and the maximum emission signal was found at 545 nm when excited at 370 nm (Figure 1.8) with a low signal-to-noise ratio around 20. This weak

fluorescence of the as-prepared FBA lead perovskite was not visible with naked eyes when irradiated with a UV lamp (365 nm). By comparing to the PEA lead perovskite which has a direct band gap, this phenomenon might be due to the significant distortion of the PbI_6^{4-} chains in FBA lead perovskite.¹¹⁷ Majority of the excited electron-hole pairs recombine through non-radiative processes at room temperature, resulting in diminished photoluminescence.

Figure 1.8. Emission spectrum of FBA lead perovskite excited at 370 nm, room temperature.

With a similar structure, the FBA lead bromide perovskite was studied by Naoki K. et al.¹¹⁶ Their work showed that the FBA has a drastically weaker PL at 408 nm compared to the PEA lead bromide perovskite, which is consistent with our results.

Furthermore, the stability of the new material was investigated. As shown in Figure 1.9, the sample was exposed to moisture over a month but remained intact which was indicated by the unchanged powder XRD pattern. These results revealed a promising improvement of stability under ambient conditions compared to the methylammonium lead triiodide (MAPbI_3).¹¹⁸ It was also reported that these fluorinated organic cations are indeed

able to improve the overall stability of perovskite solar cells, based on the studies by Wei Y. et al.^{119,120} Although the performance of these solar cells were still below satisfactory.

Figure 1.9. Powder XRD of the same FBA lead iodide sample stored under ambient conditions. No change of the pattern indicates the high stability of this material.

Due to concerns about the toxicity of lead, metal substitution of lead-based perovskites have become an important topic for the ease of further application. Moreover, lead based 2D perovskites encounter intrinsic limitations of light absorbing ability as discussed previously. Therefore, in this work, the FBA tin perovskite was synthesized and examined as a potential alternative to the FBA lead perovskite. The characterization of this new material was conducted. The results are discussed and reported herein. Some of the work is still in progress due to the air-sensitivity of the samples. A possible explanation of the sensitivity is proposed and probed.

Consistent with the hypothesis, the tin-based perovskites exhibited a wider absorption range within the visible-light region, which was verified by UV-vis DRS as shown in Figure 1.10. Compared to the lead-based perovskite, FBA tin perovskite has a

smaller band gap of 1.96 eV, which was calculated by linear fitting of the Tauc plot (Figure 1.11).

Figure 1.10. UV-Vis DRS spectrum of FBA tin perovskite. The absorption band edge appeared at 620 nm.

Figure 1.11. The Tauc plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ curve of FBA tin perovskite, with the power of $(\alpha h\nu)$ equals to $1/2$ indicating the indirect nature of the band transition. The slope of the curve was fitted by linear equation and band gap is indicated by the intersection of fitted and extrapolated line with the horizontal axis.

The structure of the FBA tin perovskite was investigated by a single crystal XRD study. The 2D layered structure is observed as shown in Figure 1.12. Similar in-plane

distortion of SnI_4^{2-} chain was observed in the crystal structure of the FBA tin perovskite, as demonstrated by a bridging bond angle of 157.9° compared to 158.0° for the lead-based sample. However, the long bond distance of the Sn-I ($3.31 \text{ \AA}$) was found to be significantly longer than that in the lead-based structure ($3.23 \text{ \AA}$), whereas the short bond distance of Sn-I ($3.07 \text{ \AA}$) was much shorter than that in the lead-based structure ($3.20 \text{ \AA}$). This difference between the Sn-I bonds indicated a mixing of I 5s orbital and I 5p orbital, which consequently interact with the Sn 5s orbitals with an inequivalent overlap. This interaction will raise the top of the valence band and increase the density of states. Together with an appreciable in-plane (*ab* plane) distortion of the SnI_4^{2-} chain, this phenomenon demonstrates one possible explanation for the further decrease of the band gap in the tin-based structure. The FBA group within the structure was further probed by FT-IR spectroscopy as shown in Figure 1.13. The characteristic amine group (N-H stretch $3500\text{-}3100 \text{ cm}^{-1}$) could be clearly seen in the spectrum which confirmed the presence of the FBA component in the structure.

Figure 1.12. 2-D single-crystal XRD structure of FBA tin perovskite. Dark grey, purple and green colors refer to Sn, I and F atoms respectively.

Figure 1.13. The FT-IR transmittance spectrum of FBA tin perovskite.

Photoluminescence experiments of FBA tin perovskite were conducted at room temperature (shown in Figure 1.14). Similar to the lead-based perovskite, only a weak fluorescence at 710 nm was observed when the sample was excited at 300 nm (4.13 eV), which likely originated from the indirect phonon-assisted band transition upon excitation.

Figure 1.14. Photoluminescence spectrum (weak signal at 710 nm) of FBA tin perovskite excited at 300 nm at room temperature. The peak at 600 nm represents the second-order diffraction in the monochromator. However, unlike the lead-based structure, the FBA tin perovskite is highly unstable under ambient conditions. The distinct red color of the powder sample darkened and turned to black within 20 minutes upon exposure to air. Therefore,

XPS data were collected to probe the possible oxidation states of Sn (shown in Figure 1.15). The sample was handled inside a glovebox with oxygen level below 1 ppm before the loading process. The data profile was then fitted for calculation which showed that 75% of the sample contained Sn(II) iodide on the surface of the sample. The rest of the Sn exhibited a higher binding energy, which indicated the existence of oxidized species with a higher oxidation state of tin. Based on this result, we proposed that the oxidation of Sn(II) is responsible for the poor stability of FBA tin perovskite. When Sn(II) is oxidized to Sn(IV), the electron pair in the Sn 5s – I 5s σ -antibonding orbital will be removed leaving the empty orbital to become the bottom of the conduction band, which results in a decrease of the band gap and could be the reason why a darkened appearance was observed during the transition process. This rapid oxidation process was determined to be inevitable during the handling of samples. In order to test a pristine sample, the loading technique must be improved.

Figure 1.15. XPS data and profile fitting of Sn (3d) of FBA tin perovskite. Peaks at 485.36 eV and 486.77 eV represent the Sn 3d_{5/2} while peaks at 493.75 eV and 495.16 eV represent the Sn 3d_{3/2}. Four components of binding energy indicate the presence of two oxidation states of Sn (75.1% Sn²⁺) on the surface of the sample according to the fitting and calculation.

The FBA tin perovskite shows a good potential to be a desirable visible-light harvester that can be applied in the artificial photosynthetic systems. But the stability has been determined to be the limit of this material for further applications. By tuning the organic part of this material, it is hypothesized that Sn(II) can be possibly stabilized by specific electron rich groups to give a new type of panchromatic, non-toxic and earth-abundant material. Work is still on going to assess this speculation.

1.3.4 (HDA)₂MI₄ perovskites

Based on the characterization and the published evaluations of FBA perovskites, attention started to steer away from these potential materials simply due to the lack of promising achievement in solar cells engineering. However, we believe that the stability of 2D perovskites can be further improved. To make perovskite more robust and water-resistant, we proposed that a long aliphatic chain in the structure could fill up the space between the two inorganic layers even more, thus blocked the attacking path of water molecule. With this assumption, we started working with 1-hexadacylamine to make a completely new type of inorganic organic hybrid perovskite. It's worth noting that a similar long-chain intercalated 2D perovskite structure was discovered but it has never been isolated and fully characterized.¹²¹ The synthesis and fundamental characterization of these innovative perovskites were conducted and documented herein.

The successful synthesis of (HDA)₂PbI₄ and (HDA)₂SnI₄ was established by single crystal X-ray diffraction (XRD) studies (Figure 1.16). Pale yellow and dark red single crystals of the respective Pb and Sn perovskites were grown by vapor diffusion of diethyl ether into THF solutions of the precursor solutions at room temperature. Remarkably, the long C₁₆ alkyl chains are stacked regularly to form the typical 2D layered structure. The (PbI₆)⁴⁻ octahedron units remain mostly undistorted in the 2D inorganic layer. The overlap

of the orbitals between Pb and I are expected to be effective, resulting in a distinct separation between the HOMOs and LUMOs, and consequently a relatively larger band-gap. The phase purity was confirmed by powder X-ray diffraction (PXRD) experiments; no HDAI or PbI_2 starting materials were observed in the diffraction data (Figure 1.17). The PXRD pattern of $(\text{HDA})_2\text{PbI}_4$ matches reasonably with the simulated pattern based on the single crystal data. Compared to the Pb counterpart, $(\text{HDA})_2\text{SnI}_4$ showed a shift of the PXRD peak positions (e.g. for the (004) and (006) planes) toward higher angles due to the smaller d -spacing (Figure 1.17).

Figure 1.16. Crystal structures of $(\text{HDA})_2\text{PbI}_4$ and $(\text{HDA})_2\text{SnI}_4$. Ellipsoid colors: Pb (blue), Sn (red), I (orange), N (pink).

Figure 1.17. PXRD patterns of $(\text{HDA})_2\text{MI}_4$ and its precursors.

The UV-vis spectrum was collected using DRS integrating sphere shown in Figure 1.18a. The absorption started from 520 nm towards the UV region and gave a peak at 483 nm within visible light region which represents the exciton absorption. The absorption of $(\text{HDA})_2\text{PbI}_4$ showed an onset at 520 nm and an exciton peak at 483 nm. $(\text{HDA})_2\text{SnI}_4$ featured a wider range starting at 605 nm with an exciton absorption around 570 nm. The band gaps are estimated to be 2.3 eV and 1.9 eV for $(\text{HDA})_2\text{PbI}_4$ and $(\text{HDA})_2\text{SnI}_4$ respectively, and both indirect in transition based on the Tauc plots calculated from the UV-vis DRS data (Figure 1.18b). The energy level from VBM to fermi level was estimated to be 2.27 eV with the help of UPS, which gives an estimated VBM energy level of 6.14 eV vs. absolute vacuum (Figure 1.19).

Figure 1.18. (a) UV-vis DRS spectra and (b) Tauc plots of the HDA Pb and Sn perovskites.

Figure 1.19. UPS spectrum of $(\text{HDA})_2\text{PbI}_4$ perovskite.

IR spectra was also collected to probe the presence of the organic groups. Characteristic alkyl group (C-H stretch $3000\text{--}2850\text{ cm}^{-1}$), amine group (N-H stretch $3500\text{--}3100\text{ cm}^{-1}$) could be clearly seen in the spectrum and no ammonium halide was found in the IR spectrum (Figure 1.20).

Elemental analysis was conducted using XPS to examine the elemental composition. The Pb $4f_{7/2}$ and $4f_{5/2}$ binding energies were 138.4 eV and 143.2 eV (Figure 1.21) respectively, consistent with a +2 oxidation state. Meanwhile, for $(\text{HDA})_2\text{SnI}_4$, Sn(II) was confirmed as the sole species with binding energies at 485.6 eV and 494.0 eV for $3d_{5/2}$ and

$3d_{3/2}$, respectively (Figure 1.22). $I\ 3d_{5/2}$ and $3d_{3/2}$ were found at 618.3 eV and 629.8 eV as distinctive I^- species. N 1s was found at 401.4 eV being recognized as a typical alkyl ammonium cation.

Figure 1.20. FT-IR spectra of HDA based perovskites and HDAI salt.

Figure 1.21. The XPS spectra of $(HDA)_2PbI_4$ perovskite.

Figure 1.22. The XPS spectra of $(\text{HDA})_2\text{SnI}_4$ perovskite.

Besides X-ray diffraction and photoelectron spectroscopic characterization, scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) was employed (Figure 1.23) to confirm that the $(\text{HDA})_2\text{PbI}_4$ solid produced is a homogenous phase. The SEM studies revealed that the mechanochemically synthesized powder is composed of micron sized particles, and elemental mapping showed that it is indeed a homogenous phase.

Figure 1.23. SEM image and elemental mappings of $(\text{HDA})_2\text{PbI}_4$.

The as-prepared $(\text{HDA})_2\text{PbI}_4$ perovskite was found to give off a strong light emission under UV irradiation (365 nm). Then PL spectroscopy was used to examine the photoluminescence property. A distinct emission peak at 498 nm was found when excited at 350 nm, as shown in Figure 1.24. A significant color change of PL was observed when cooled down with liquid N_2 . The photoluminescence property at lower temperatures was

investigated using VT-PL technique, and the results will be discussed later. At this point, two hypotheses can be proposed: the binding energy of excitons increases when the temperature drops; increased strength of lead halide bonds are expected at low temperatures resulting in a stronger interaction between overlapping orbitals, leading to a wider energy gap between HOMO and LUMO of lead halide complexes, which is a typical Varshni behavior observed in regular semiconductors. Most interestingly, it was noticed that $(\text{HDA})_2\text{PbI}_4$ was still emissive when irradiated with UV while suspended in water, as shown in Figure 1.24. However, $(\text{HDA})_2\text{SnI}_4$ did not exhibit the same stability, likely due to the rapid oxidation of Sn(II) to Sn(IV). The 2D structure and the hydrophobic nature of FBA and HDA do not inhibit this oxidation process, leaving these Sn(II)-based materials vulnerable to oxygen. One hypothesis to stabilize the Sn(II) is to introduce strong electron rich additives or dopants to prevent the oxidation of Sn(II).

Figure 1.24. Steady-state PL spectra of $(\text{HDA})_2\text{PbI}_4$ water suspension excited at 350 nm.

Regardless of the high intensity, the lifetime of photoluminescence was surprisingly short, only 0.423 ns in average according to TCSPC data (Figure 1.25). This short lifetime might be due to the lack of long-range crystalline structure and less density of states of the 2D sheet structure. The lifetime would be expected to be drastically longer when sample is

well crystalized in larger size according to the work on MAPbI₃ by Valerio D.I et al,¹²² and work is still in progress to obtain a large size crystal sample in cm scale.

Figure 1.25. Data plot of TCSPC. Raw data was fitted with a biexponential decay function.

The long chain alkyl group was expected to be an effective water repelling functionality within the perovskite structure. HDA lead perovskite was able to stay intact in direct contact with water (Figure 1.24). It was also noticed that this perovskite was able to crystalize and suspend in aqueous media as a nanocrystal solution. The density of this perovskite dramatically decreases while introducing long chain alkyl group regardless of the presence of heavy lead metallic atom. The low density of this material originates from the spacious crystal lattice and contributes to the strong water repelling property. The stability of these perovskites was tested subsequently under humid atmospheric conditions. (HDA)₂PbI₄ formed a suspension in water, with some larger pieces of the material afloat on the surface. The PXRD pattern of the sample after stirring for 30 min in water was indistinguishable from the pristine (HDA)₂PbI₄ (Figure 1.25). The hydrophobicity was evaluated by Contact angle (CA) measurements also confirmed the hydrophobicity with an average angle of 98.4° (Table 2.1, Figure 1.26) that is significantly higher than 90°. This

result showcases a drastic improvement of hydrophobicity compared with the contact angels of 50.3° for MAPbI_3 and 69.9° Mg doped MAPbI_3 , reported by Yang. F et al.⁷³

Figure 1.25. PXRD pattern of $(\text{HDA})_2\text{PbI}_4$ before (below) and after (top) suspending in water (100 mg in 1 mL).

Table 1.1. Data from contact angle measurements.

EXPERIMENT	1	2	3	4	5	AVG.	σ
ANGLE ($^\circ$)	101.85	105.99	93.83	92.44	97.92	98.4	5.61

Figure 1.26. Photograph of a contact angle measurement.

Interesting nanoscale structure was observed under TEM as shown in Figure 1.27. The solution of the product in THF was drop into pentane or hexane to give a diluted suspension, which was prepared as the sample for TEM. The sample exhibited a long rod shape (over 2.0 micrometers) with tunnels inside (about 40 nm diameter wide). The forming of this unique morphology could be explained by the solvent-extraction process similar to the work by Tom K. et al.¹²³ THF would be extracted by hexane and pentane leaving a solvent path which could be the origin of porous structure and tunneling. It gave an insight

on the fabrication of perovskite with nanoscale porous structure, which will be an intriguing feature for the fabrication of photovoltaic devices. This mesoporous structure creates short pathway to the surface of material, which provides more active sites and facilitates charge separation. Meanwhile, this hallow structure makes it possible for perovskite to become a supporting framework to host other hierarchy components while assembling up to an integrated nano composite. These integrated composite materials are expected to be very promising candidates for photosensitizers in artificial photosynthetic systems due to the improved electron transfer along the energy levels within different components. The investigation of these integrated systems is still ongoing as a prospective research direction.

Figure 1.27. TEM images of HDA lead perovskite. Prepared by THF solution in hexane.

To further investigate the photophysical properties of $(\text{HDA})_2\text{PbI}_4$ perovskite, we conducted VTPL measurements down to liquid N_2 temperature. As shown in Figure 1.28a, a significant blue shift was observed upon cooling below 300 K. It is expected that the Pb-I bonds will contract at those low temperatures, resulting in a stronger interaction between overlapping orbitals, a higher Pb-I bond strength, and a wider energy gap between the valence and conduction bands, which is due to typical Varshni effect observed in regular semiconductors.¹²⁴ Time-resolved PL (TRPL) studies were also performed at variable

temperatures. The PL decay transients from 80 to 300 K could be consistently fitted bi-exponentially, suggesting the presence of two decay processes, albeit with different weighting. The faster process (0.32 ± 0.01 to 0.17 ± 0.01 ns) likely originated from the exciton recombination in the defects rich region, while the slower process (3.0 ± 0.01 to 1.5 ± 0.01 ns) could arise from the exciton recombination with fewer defects around. The PL lifetime become longer with reducing the temperatures, indicating the suppression of the thermal assisted non-radiative trapping process by defects at higher temperatures (Figure 1.28c). These results indicated a sufficiently long lifetime of the excited species (longer than the diffusion limit which is about 1 ns) for electron extraction after photoexcitation. Additionally, the intensity of PL increases nearly linearly when temperature goes up, which indicated the nature of defect trap assisted recombination.

Figure 1.28. (a) VTPL and (b) VT-TRPL spectra of (HDA)₂PbI₄ after exciting at 390 nm. (c) Lifetimes of the two processes at different temperatures. (d) PL intensity at different temperatures.

In addition, it was helpful to determine the valence band maximum (VBM) as 5.70 eV (Figure 1.29) by photoelectron spectroscopy in air (PESA), which corresponded to a potential of 1.20 V vs. NHE. This result indicated the relatively strong oxidizing nature of the catalysts. The aggregate characterization suggested a potential application of (HDA)₂PbI₄ as a visible-light photosensitizer for oxidation reactions.

Figure 1.29. PESA data of (HDA)₂PbI₄ with the intercept at the abscissa for the estimated VBM.

1.4 Photoredox catalysis

As a type of cost-effective materials based on earth abundant elements, it has been highly anticipated to apply perovskites in synthesis and catalysis. Therefore, by developing the above 2D perovskites, we aimed to explore their potentials in this blooming field. In the realm of photocatalysis, oxidation reactions with air are highly desirable due to increasing concern in the use of energy-intensive and stoichiometric oxidants. Among them, dehydrogenation and decarboxylation reactions are attractive for the purposes of H₂ storage

and C-C coupling synthesis respectively.¹²⁵ Moreover, carboxylic acids are ubiquitous in natural products and widely used as basic building blocks in both industrial and pharmaceutical synthesis.¹²⁶ Thus, photocatalytic oxidative decarboxylation presents a convenient approach to cleave a carbon-carbon bond to access valuable intermediates or products.^{15,127}

It was firstly found that our perovskite was able to oxidize ferrocene to ferrocenium in a stoichiometric fashion, which gives a distinctive color change and the broadening of NMR peaks. Decamethylferrocenium was synthesized to probe the reduction ability of the catalyst as a reverse reaction, the NMR signal of ferrocene was observed as a broad and shifted peak. However, the reaction did not proceed to complete conversion despite the increase of catalyst loading. The later exploration involved some other substrates that are easy to oxidize, including ethyl vinyl ether, 1,4-cyclohexadiene and thiophenols. DE was found as the oxidized product from ethyl vinyl ether which indicates the oxidation process clearly. Cyclohexadiene underwent dehydrogenation when the catalyst was charged to the reaction mixture yielding benzene as a product detected in NMR spectrum. Disulfides was found as products when thiophenols were exposed to white LED irradiation with the presence of catalyst.

Figure 1.30. Photographs of the white LED lamp (left) and the setup (right) for photoredox reactions. The temperature of the water bath remains almost constant around 26 °C.

Moving on, it was found that indoline-2-carboxylic acid underwent decarboxylation to form indoline in the presence of (HDA)₂PbI₄ under N₂ and irradiation from a 48 W white LED lamp. On the other hand, both decarboxylation and dehydrogenation to indole occurred with the additional presence of O₂. Control experiments were performed to validate the necessity of (HDA)₂PbI₄ and visible light irradiation for the decarboxylation reaction (Table 1 entries 2-7). Regardless of the photoactive nature, PbI₂ did not catalyze the reaction effectively (entry 3). Both electron-deficient (Br and Cl substituted) and electron-rich substrates (methyl substituted) underwent decarboxylation to their corresponding indoline products in high yields (entries 9-11, 13). The catalyst could be recovered after the reaction in its original form, which was confirmed by the PXRD result (Figure 1.31).

Table 1.2. Representative decarboxylation and dehydrogenation reactions catalyzed by the Pb and Sn 2D perovskites.

Entry	A	B	C	M	Condition	Yield (%)	
					variations	indoline	indole
1	H	COOH	-	Pb	-	98	-
2	H	COOH	-	-	with HDAI	14	-
3	H	COOH	-	-	with PbI ₂	2	-
4	H	COOH	-	-	with I ₂	0 ^[a]	-

5	H	COOH	-	Pb	no light	1	-
6	H	COOH	-	-	no cat.	4	-
7	H	COOH	H	Pb	40 °C ^[b]	0	0
8	H	COOH	H	Pb	O ₂	-	78
9	Br	COOH	-	Pb	-	81	-
10	Br	COOH	H	Pb	O ₂		84
11	Cl	COOH	-	Pb	-	81	-
12	Cl	COOH	H	Pb	O ₂	-	20
13	Me	COOH	-	Pb	-	83	-
14	Me	COOH	-	Sn	-	30	-
15	Me	COOH	H	Pb	O ₂	-	<10
16	CF ₃	H	H	Pb	O ₂	-	48
17	H	Me	Me	Pb	O ₂	-	17
18	H	Me	Me	Pb	DE, O ₂	-	71
19	H	Me	Me	Sn	DE, O ₂	-	47

^[a]11% conversion to unknown product. ^[b]Up to the boiling point of DCM (40 °C at 1 atm.).

Figure 1.31. PXRD pattern of the recovered (HDA)₂PbI₄ after the reaction, with comparison to a fresh prepared sample, HDAI and PbI₂. The small additional peaks are likely due to the minor decomposition of the catalyst and other unidentifiable intermediates.

Furthermore, 5-trifluoromethylindoline and 2-methyl-indoline were evaluated as substrates for dehydrogenation, yielding 48% and 17% of the respective indoles (entries 16, 17). By using DE as a solvent, the yield of 2-methylindole could be raised to 71% (entry 18). We also explored photocatalysis by the lead-free (HDA)₂SnI₄ congener, but the decarboxylation of 5-methylindoline acid yielded 30% of the indoline (entry 14), while the dehydrogenation of 2-methyl-indoline led to a 47% yield of the indole in DE (entry 19). These moderate yields are likely due to the oxidative instability and abundance of traps for Sn(II) perovskites. With the guidance by previous reports on photoredox catalysis,^{91,126} the propose mechanisms for the decarboxylation and dehydrogenation are shown in Scheme 1. To verify the speculation, ferrocene was applied as a hole scavenger and it impeded the decarboxylation reaction completely. On the other hand, AgBF₄ was used as a sacrificial electron acceptor and it had no effect to the reaction indicating the rate determining role of the preceding electron transfer process facilitated by our catalysts. For the model dehydrogenation reaction, the yield was reduced to 32% with the excessive presence of tiron (disodium 4,5-dihydroxy-1,3-benzenedisulfonate-4,5-dihydroxy-1,3-benzenedisulfonate) as a superoxide scavenger¹²⁸ which revealed the presence and rate-determining role of the superoxide radical intermediate illustrated in the proposed mechanism (Scheme 1.1). Finally, an “on-off” irradiation study was conducted (Figure 1.32) to exclude a radical chain mechanism.

Scheme 1.1. Proposed mechanisms for the decarboxylation (left) and dehydrogenation (right) reactions. [P] represents the perovskite photocatalysts.

Figure 1.32. “On-off” tests of the indoline-2-carboxylic acid decarboxylation.

1.5 Conclusions

This chapter highlights a synthetic work on the design and synthesis of new 2D perovskites with improved stability under ambient conditions. A feasible synthetic approach was successfully developed using THF as a solvent instead of other high boiling point solvents. For the application in artificial photosynthetic system, to synthesize and examine

perovskites that are stable under ambient conditions are the main objectives of this project. HDA and FBA based perovskites were studied and are documented herein. The properties of these new perovskites were examined and discussed. As the results indicate, the lead-based perovskite demonstrates significantly improved stability under ambient conditions, while the tin-based perovskite exhibits a wider range of visible-light absorption with more desirable band gaps. The stability of tin based perovskites needs to be further investigated to gain a better understanding. Further electrochemistry experiments are needed to evaluate the capability of these new materials in organic solvents for applications in artificial photosynthesis. In the following studies, it was decided to focus on the HDA based perovskites due to their high novelty and intriguing properties with the potential to become a game-changer in the realm of hybrid metal halide perovskites. The detailed characterization of these new perovskites was conducted with highlighting some of the valuable features of these materials for photoredox catalysis. Notably, their marked phase stability when suspended in organic solvents, even in the presence of protic sources such as water, provided the opportunity to utilize them for organic synthesis. As a conceptual demonstration, $(\text{HDA})_2\text{PbI}_4$ and $(\text{HDA})_2\text{SnI}_4$ were found able to effect the photocatalytic redox-neutral decarboxylation and oxidative dehydrogenation of indoline carboxylic acids. This work showcases another original application for the flourishing portfolio of the hybrid organic-inorganic halide perovskites and paves the way for their wider utilization in photoredox organic synthesis.

1.6 Crystallographic data

Table 1.3. Crystallographic data for FBA lead perovskite.

Chemical formula	C₁₄H₁₈F₂I₄N₂Pb	
Formula weight	967.09 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.060 x 0.080 mm	
Crystal habit	orange plate	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.7029(2) Å	$\alpha = 90^\circ$
	b = 9.2474(3) Å	$\beta = 97.5595(16)^\circ$
	c = 27.5808(8) Å	$\gamma = 90^\circ$
Volume	2200.39(11) Å ³	
Z	4	
Density (calculated)	2.919 g/cm ³	
Absorption coefficient	13.295 mm ⁻¹	
F(000)	1712	
Theta range for data collection	2.33 to 31.19°	
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -40 ≤ l ≤ 38	
Reflections collected	60128	
Independent reflections	7112 [R(int) = 0.0629]	
Coverage of independent reflections	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7770 and 0.4160	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7112 / 0 / 210	
Goodness-of-fit on F²	1.054	
$\Delta/\sigma_{\max}$	0.001	

Final R indices	5816 R1 = 0.0273, wR2 = 0.0505 data; I>2σ(I) all data R1 = 0.0402, wR2 = 0.0542
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0176P) ² +5.9563P] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	1.700 and -2.547 eÅ ⁻³
R.M.S. deviation from mean	0.215 eÅ ⁻³

Table 1.4. Crystallographic data for FBA tin perovskite.

Chemical formula	C₁₄H₁₈F₂I₄N₂Sn	
Formula weight	878.59 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.100 x 0.140 mm	
Crystal habit	red plate	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.6725(5) Å	α = 90°
	b = 9.2069(5) Å	β = 97.6163(18)°
	c = 27.5194(13) Å	γ = 90°
Volume	2178.0(2) Å ³	
Z	4	
Density (calculated)	2.679 g/cm ³	
Absorption coefficient	6.859 mm ⁻¹	
F(000)	1584	
Theta range for data collection	2.34 to 31.04°	
Index ranges	-12<=h<=12, -13<=k<=12, -39<=l<=39	
Reflections collected	29872	
Independent reflections	6962 [R(int) = 0.0602]	
Coverage of independent reflections	99.8%	

Absorption correction	multi-scan	
Max. and min. transmission	0.8750 and 0.4470	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6962 / 0 / 210	
Goodness-of-fit on F^2	1.053	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	5591 data; $I > 2\sigma(I)$	R1 = 0.0393, wR2 = 0.0664
	all data	R1 = 0.0550, wR2 = 0.0711
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0088P)^2 + 6.9001P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	1.355 and -1.548 eÅ ⁻³	
R.M.S. deviation from mean	0.250 eÅ ⁻³	

Table 1.5. Sample and crystallographic data for (HDA)₂PbI₄ perovskite (CCDC 1856671).

Identification code	shs88
Chemical formula	C ₃₂ H ₇₂ I ₄ N ₂ Pb
Formula weight	1199.70 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.060 x 0.120 x 0.160 mm
Crystal system	orthorhombic
Space group	P c a 21
Unit cell dimensions	a = 8.3545(16) Å α = 90° b = 59.657(11) Å β = 90° c = 8.6608(16) Å γ = 90°
Volume	4316.6(14) Å ³
Z	4
Density (calculated)	1.846 g/cm ³
Absorption coefficient	6.790 mm ⁻¹
F(000)	2288
Theta range for data collection	2.39 to 29.72°
Index ranges	-11 ≤ h ≤ 10, -62 ≤ k ≤ 83, -11 ≤ l ≤ 12
Reflections collected	48558
Independent reflections	11765 [R(int) = 0.1025]
Absorption correction	Multi-Scan
Max. and min. transmission	0.6860 and 0.4100
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)

Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Data / restraints / parameters	11765 / 217 / 357
Goodness-of-fit on F^2	1.024
$\Delta/\sigma_{\max}$	0.002
Final R indices	8860 data; $I > 2\sigma(I)$ $R1 = 0.0795$, $wR2 = 0.1558$ all data $R1 = 0.0795$, $wR2 = 0.1558$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0725P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Absolute structure parameter	0.516(11)
Largest diff. peak and hole	3.106 and -1.710 eÅ ⁻³
R.M.S. deviation from mean	0.308 eÅ ⁻³

Table 1.6. Sample and crystallographic data for (HDA)₂SnI₄ (CCDC 1856670).

Identification code	shs115s	
Chemical formula	C ₃₂ H ₇₂ I ₄ N ₂ Sn	
Formula weight	1111.20 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.010 x 0.200 x 0.220 mm	
Crystal habit	red plate	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 8.3549(11) Å	α = 90°
	b = 8.5625(11) Å	β = 90°
	c = 60.398(8) Å	γ = 90°
Volume	4320.8(10) Å ³	
Z	4	
Density (calculated)	1.708 g/cm ³	
Absorption coefficient	3.470 mm ⁻¹	
F(000)	2160	
Theta range for data collection	2.53 to 27.19°	
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 8, -77 ≤ l ≤ 58	
Reflections collected	19684	
Independent reflections	4677 [R(int) = 0.0527]	
Coverage of independent reflections	97.1%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9660 and 0.5160	
Refinement method	Full-matrix least-squares on F ²	

Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Data / restraints / parameters	4677 / 6 / 180
Goodness-of-fit on F^2	1.468
$\Delta/\sigma_{\max}$	0.001
Final R indices	3992 data R1 = 0.0868, wR2 = 0.1899 I>2 σ (I)
	all data R1 = 0.0994, wR2 = 0.1932
Weighting scheme	$w=1/[\sigma^2(F_o^2) + 181.1755P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.094 and -4.271 eÅ ⁻³
R.M.S. deviation from mean	0.280 eÅ ⁻³

1.7 Materials and instrumental details

Materials

Compound 1-hexadecylamine (HDA, 98%) was purchased from Merck and used without purification. Hydroiodic acid (HI, 57% wt. aq.) was purchased from TCI. PbI₂ (99.999%) was purchased from Sigma-Aldrich. SnI₂ was purchased from Strem and stored in a glove box in a N₂ atmosphere. Indoline-2-carboxylic acid (98%) was purchased from Apollo and stored in a glove box. Compounds 5-chloroindoline-2-carboxylic acid hydrochloride monohydrate (Sigma-Aldrich, 99%) and 5-methylindoline-2-carboxylic acid hydrochloride (Sigma-Aldrich, 99%) were treated with NaHCO₃ under N₂ to remove HCl to provide the respective substrates 5-chloroindoline-2-carboxylic acid and 5-methylindoline-2-carboxylic acid before usage. Dichloromethane was desiccated using CaH₂, degassed, and stored in a

glove box before use. Tetrahydrofuran (THF) was distilled and stored in a glove box to minimize the moisture and O₂ contents.

Instrumental details

UV-visible diffuse reflectance spectroscopy (UV-vis DRS). UV-vis DRS spectra were acquired using a Shimadzu UV-3600 UV-vis spectrometer with an integrating sphere (Shimadzu ISR-3100). The samples were mixed with barium sulfate powder as the optical reference standard and packed into a sample holder for the scan.

Fourier-transform infrared spectroscopy (FTIR). FTIR spectra were acquired using a Bruker VERTEX 80v infrared spectrometer with an attenuated total reflection (ATR) accessory. The atmosphere of the specimen compartment was purged with N₂ for over 30 min after sample mounting. Air-sensitive samples were analyzed in a glovebox under a N₂ atmosphere.

Powder X-ray diffraction (PXRD). PXRD experiments were conducted using a Bruker D8 Advance X-ray diffractometer with a copper (K_{α1} (1.5406)/K_{α2} (1.5444) = 2) target X-ray tube set to 40 kV and 40 mA. Air-sensitive samples were prepared and loaded into an air-tight specimen holder purchased from Bruker (A100B33) in a glovebox before analysis.

X-ray photoelectron spectroscopy (XPS). XPS data were acquired using a Phoibos 100 spectrometer and a Mg X-ray source (SPECS, Germany) working at 12.5 kV equipped with dual Al/Mg anodes. The O 1s signal was also prominent in the XPS spectra due to the use of a carbon tape to attach samples onto the specimen plates.

Photoluminescence (PL) experiments. PL spectra were acquired using a Varian Cary Eclipse fluorescence spectrophotometer. Variable temperature PL (VTPL) studies were carried out and ultrafast femtosecond optical spectroscopic methods were employed to measure the VTPL data and the full width at half maximum (FWHM) of the crystal flakes. Samples were contained in an encapsulation equipped with liquid N₂ circulation. A

Coherent Libra regenerative amplifier (50 fs, 1 kHz, 800 nm) seeded by a Coherent Vitesse Oscillator (100 fs, 80 MHz) were used as the pump laser sources. For pump wavelength tuning, the Coherent OPerA Solo optical parametric amplifier was used. Upon optically pumping the samples, the respective PL emissions were collected at a backscattering angle of 150° by a collimating lens pair, guided into an optical fiber that was coupled to a spectrometer (Acton, SpectraPro 2500i and SP2300), and detected by a charge coupled device (CCD; Princeton Instruments, Pixis 400B). Time-resolved PL (TRPL) was collected using an Optronis Optoscope streak camera system. The fitting was done according to the following equation:

$$y = y_0 + A_1 * \exp\left(-\frac{x-x_0}{t_1}\right) * \left(1 - \operatorname{erf}\left(-\frac{x-x_0-\frac{s^2}{t_1}}{s}\right)\right) + A_2 * \exp\left(-\frac{x-x_0}{t_2}\right) * \left(1 - \operatorname{erf}\left(-\frac{x-x_0-\frac{s^2}{t_2}}{s}\right)\right)$$

with x_0 and y_0 as the intercept on the axes, A as the amplitude of each component, s as the response time, erf as the error function, t_1 and t_2 as the lifetimes derived from the fitting results.

Photoelectron spectroscopy in air (PESA). PESA was conducted with Model AC-2 from RKI Instruments with the ultra-violet light intensity set at 10.0 nW. The samples were attached onto glass plates using carbon tape.

Details of substrates syntheses and photocatalytic studies

Decamethylferrocene (FeCp₂*): Cp* (0.51 mL, purified by distillation at 35 °C 3 mbar) was mixed with *n*-butyllithium (5.0 mL, 1.0 M in hexane, dropwise addition) in 20 mL anhydrous THF in an ice-bath. The mixture was left stirring overnight, cooled with dry ice

IPA bath, followed by the addition of anhydrous FeCl₂ (209 mg suspended in 20 mL THF) via a needle and a syringe. The resulting mixed was allowed to warm up to room temperature and refluxed under N₂ at 70 °C for 12 h. The crude product was collected after removing the solvent under vacuum, then purified by sublimation at 160 °C under vacuum. A yellow crystalline solid was collected as the final product (0.33 g, 61% yield). [FeCp₂*]⁺ was synthesized by mixing FeCp₂* with AgBF₄ in DCM and used after recrystallization in toluene.

Compound 5-bromoindoline-2-carboxylic acid: The synthesis was reproduced as previously reported.¹²⁹ Indoline-2-carboxylic acid (163 mg, 1.00 mmol) was dissolved in 2.0 mL of *N,N*-dimethylformamide and cooled with an ice-salt bath. NBS (178 mg, 1.00 mmol) was added with vigorous stirring. The resulting mixture was stirred for 2 h before 10 mL of water was added. The resulting suspension was transferred into a separating funnel and the crude product was extracted by 10 mL of ethyl acetate for three times. The organic portions were combined, washed with water twice, dehydrated with MgSO₄ and concentrated under vacuum. The crude product was recrystallized in pentane to give a pale yellow solid (128 mg, 53% yield). ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 3.09 (dd, *J* = 16.5, 5.6 Hz, 1 H), 3.27 (dd, *J* = 16.5, 10.6 Hz, 1 H), 4.30 (dd, *J* = 10.6, 5.6 Hz, 1 H), 6.50 (d, *J* = 8.3 Hz, 1 H), 7.06 (d, *J* = 8.3 Hz, 1 H), 7.14 (s, 1 H) ppm. MS (ESI⁺, *m/z*) calculated for C₉H₉BrNO₂ [M + H]⁺ 241.97, found 241.99.

Photocatalytic studies

All the photocatalytic experiments were carried out in 25 mL reaction tubes that were sealed under a N₂ atmosphere. For the reactions with O₂, the reaction mixtures were cooled with liquid N₂ until the solvents froze, degassed under vacuum and refilled with O₂. The reaction mixtures were then exposed to visible light radiation under a white LED lamp (equipped with a 48 W LED chip and a cooling fan) with vigorous stirring. The products were collected

by removing the solvents under vacuum. Dibromomethane (2 H at $\delta = 5.41$ in DMSO- d_6) was used as an internal standard to calculate the yield by NMR spectroscopy.

NMR data for the substrates in photocatalytic studies:

Entries 1 – 7: Indoline, ^1H NMR (DMSO- d_6 , 400 MHz): $\delta = 2.92$ (t, $J = 8.4$ Hz, 2 H), 3.42 (t, $J = 8.4$ Hz, 2 H), 6.59 (t, $J = 7.6$ Hz, 2 H), 6.93 (t, $J = 7.5$ Hz, 1 H), 7.05 (d, $J = 7.1$ Hz, 1 H) ppm. GC-MS m/z calculated for $\text{C}_8\text{H}_9\text{N}$ [M] m/z 119.07, found 119.10.

Entry 7-8: Indole, ^1H NMR (DMSO- d_6 , 400 MHz): $\delta = 6.42$ (m, 1 H), 6.98 (t, $J = 7.4$ Hz, 1 H), 7.07 (t, $J = 7.5$ Hz, 1 H), 7.32 (t, $J = 2.7$ Hz, 1 H), 7.39 (d, $J = 8.1$ Hz, 1 H), 7.53 (d, $J = 7.8$ Hz, 1 H) ppm. GC-MS m/z calculated for $\text{C}_8\text{H}_7\text{N}$ [M] m/z 117.06, found 117.08.

Entry 9: 5-bromoindoline, ^1H NMR (DMSO- d_6 , 400 MHz): $\delta = 2.93$ (t, $J = 8.5$ Hz, 2 H), 3.44 (t, $J = 8.5$ Hz, 2 H), 6.49 (d, $J = 8.2$ Hz, 1 H), 7.05 (d, $J = 7.5$ Hz, 1 H), 7.17 (s, 1 H) ppm. GC-MS m/z calculated for $\text{C}_8\text{H}_8\text{BrN}$ [M] m/z 196.98, found 197.00

Entry 10: 5-bromoindole, ^1H NMR (DMSO- d_6 , 400 MHz): $\delta = 6.40 - 6.43$ (m, 1 H), 7.18 (d, $J = 8.5$ Hz, 1 H), 7.31 – 7.50 (m, 2 H), 7.72 (s, 1 H) ppm. GC-MS m/z calculated for $\text{C}_8\text{H}_6\text{BrN}$ [M] m/z 194.97, found 194.97.

Entry 11: 5-chloroindoline, ^1H NMR (DMSO- d_6 , 400 MHz): δ = 2.94 (t, J = 8.5 Hz, 2 H), 3.46 (t, J = 8.5 Hz, 2 H), 6.58 (d, J = 8.3 Hz, 1 H), 6.91 – 6.99 (m, 1 H), 7.04 – 7.11 (m, 1 H) ppm. GC-MS m/z calculated for $\text{C}_8\text{H}_8\text{ClN}$ [M] m/z 153.03, found 153.05.

Entry 12: 5-chloroindole, ^1H NMR (DMSO- d_6 , 400 MHz): δ = 6.61 – 6.64 (m, 1 H), 7.04 (dd, J = 2.01, 8.6 Hz, 2 H), 7.37 (d, J = 8.6 Hz, 1 H), 7.53 (d, J = 2.1 Hz, 1 H) ppm. GC-MS m/z calculated for $\text{C}_8\text{H}_6\text{ClN}$ [M] m/z 151.02, found 151.01.

Entry 13-14: 5-methylindoline, ^1H NMR (DMSO- d_6 , 400 MHz): δ = 2.16 (d, J = 5.6 Hz, 3 H), 2.86 (t, J = 8.4 Hz, 2 H), 3.38 (t, J = 8.4 Hz, 2 H), 6.46 (d, J = 8.4 Hz, 1 H), 6.72 (d, J = 7.8 Hz, 1 H), 6.86 (s, 1 H) ppm. GC-MS m/z calculated for $\text{C}_9\text{H}_{11}\text{N}$ [M] m/z 133.09, found 133.11.

Entry 15: 5-methylindole, ^1H NMR (DMSO- d_6 , 400 MHz): δ = 2.40 (s, 3 H), 6.75 (d, J = 2.4 Hz, 1 H), 7.06 (d, J = 9.3 Hz, 1 H), 7.32 (d, J = 8.5 Hz, 1 H), 7.39 (s, 1 H), 7.46 (d, J = 2.5 Hz, 1 H) ppm. GC-MS m/z calculated for $\text{C}_9\text{H}_9\text{N}$ [M] m/z 131.07, found 131.09.

Entry 16: 5-trifluoromethylindole, ^1H NMR (DMSO- d_6 , 400 MHz): δ = 6.53 – 6.59 (m, 1 H), 7.22 – 7.29 (m, 1 H), 7.59 (t, J = 2.7 Hz, 1 H), 7.69 (m, 2 H) ppm. ^{19}F NMR (DMSO-

d_6 , 376 MHz): $\delta = -61.24$ ppm. GC-MS m/z calculated for $C_9H_6F_3N$ [M] m/z 185.05, found 185.06.

Entry 17-19: 2-methylindole, 1H NMR ($DMSO-d_6$, 400 MHz): $\delta = 2.38$ (s, 3 H), 6.08 – 6.13 (m, 1 H), 6.85 – 6.98 (m, 2 H), 7.25 (t, $J = 7.4$ Hz, 1 H), 7.37 (d, $J = 7.2$ Hz, 1 H) ppm. GC-MS m/z calculated for C_9H_9N [M] m/z 131.07, found 131.09.

Chapter II

Solvent-Free, Kilogram-Scale, Mechanochemical Synthesis of Phase-Pure, Metastable Metal Halide Perovskites

This chapter is adapted from a work that is currently under review for publication. The authors include Zonghan Hong, Davin Tan, Rohit Abraham John, Yong Kang Eugene Tay, Yan King Terence Ho, Tze Chien Sum, Nripan Mathews, Felipe García, and Han Sen Soo. The author of this thesis contributed in the major part of this work. H.S.S., F.G., and N.M. conceived the research. H.S.S. and F.G. obtained the funding for the project and jointly supervised Z.H. and D.T. Z.H. and D.T. designed the experiments. Z.H., D.T., and Y.K.T.H. performed the synthetic and characterization experiments, and conducted the photophysical measurements. R.A.J. collected the photoelectrical data and analyzed the results. Y.K.E.T collected the PL and TRPL data and analyzed the results.

ABSTRACT: Mechanochemistry is a green, solid-state, re-emerging synthetic technique that can rapidly and efficiently form complex molecules and materials without exogenous heat or solvent(s). Herein, we report the application of solvent-free mechanochemical ball milling for the synthesis of metal halide perovskites, to overcome problems with solution-based syntheses like phase impurity, high preparation temperatures, and poor reagent solubilities. We prepared phase-pure, air-sensitive CsSnX_3 ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) and their mixed halide perovskites by reactions between cesium and tin(II) halides. Notably, even metastable, high temperature phases such as cubic CsSnCl_3 , cubic CsPbI_3 , and trigonal FAPbI_3 were accessible at ambient temperatures. The perovskites can be prepared up to kilogram scales. Photodetector devices based on $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ were then fabricated using the mechanosynthesized perovskites under solvent-free conditions and showed significant ten-fold differences between on/off currents. We highlight a unique, large-scale, and essentially solvent-free, general approach to synthesize metastable compounds and even to fabricate devices for sustainable energy applications.

2.1 Introduction

Mechanochemistry is a re-emerging, green, solid-state synthetic technique that can rapidly provide access to complex small molecules or new materials, without the need to introduce solvents or heat. Lately, metal halide perovskites have been considered as one of the top choices for future solar cells and optoelectronic devices. With the expected high demand for perovskite materials and devices, a solvent-free, mechanochemical, ball-milling approach has been developed to synthesize technologically relevant and even metastable perovskites up to kilogram scales, and created photodetector devices without any solvents, all conducted under ambient conditions. In this chapter, this unique solvent free method was used to prepare lead- and tin-variants with high phase- and compositional-purity directly from their solid metal halide precursors. Our essentially solvent-free, general method can reduce the energy and environmental footprint of materials synthesis and device fabrication, which can potentially be incorporated into future industry solutions.

Figure 2.1. (a) Reaction scheme for the ball milling reaction to form all-inorganic tin perovskites using CsX and SnX_2 ($\text{X} = \text{Cl, Br, I}$). The three-ball symbol above the arrow

represents the mechanochemical procedure. The powders were prepared in a N₂ filled glovebox, sealed in air-tight vessels, and then milled for 60 min. The key advantages of performing such mechanochemical ball milling synthesis are highlighted in green. (b) Photographs depicting the reagents before and after milling on 200 mg scales. (c) Photograph of a 250 g scale reaction of the mixed halide perovskite CsSnBr_{1.5}Cl_{1.5} after 10 h of milling.

2.2 Results and discussion

2.2.1 Solvent-free, mg- to kg-scale syntheses of phase-pure perovskites

As a preliminary reaction on a 200 mg scale, CsI and SnI₂ were placed in a 10 mL stainless steel jar with a 1:1 stoichiometric ratio (Figure 2.1a), along with one 10 mm 4.0 g stainless steel ball providing a ball to reagent ratio (BRR) of 20. The reaction was set up in an inert N₂ glovebox to prevent the oxidation of Sn(II) to Sn(IV), sealed and removed from the glovebox, and was subsequently placed in a vibration mill. After 60 min of oscillation at 30 Hz, the solids were collected from the reaction vessel in a glovebox – without annealing or further purification – and the uniformly colored product was characterized using powder X-ray diffraction (PXRD), which is quintessential for qualitative evaluation of the products. As shown in Figure 2.2a, the PXRD pattern of the product matched perfectly with that of the previously reported black orthorhombic polymorph of CsSnI₃ perovskite and did not show other crystalline impurities (*e.g.*, precursors, decomposition products, or other polymorphic phases). Such phase purity in metal halide perovskites is in stark contrast with solution-based methods, since prior syntheses typically included a mixture of phases as well as signs of decomposition.¹³⁰

Figure 2.2. Comparison of the PXRD patterns of CsSnI₃ perovskite synthesized by: (a) mechanochemical ball milling, (b) temperature-controlled interval milling, (c) cryomilling under liquid N₂, and (d) heating of the solid reagents in a sand bath up to 320 °C under Ar. For reference, the PXRD patterns of the starting materials (e) SnI₂ and (f) CsI are shown. (g) Comparison of the XPS data of the pristine, mechanochemically synthesized CsSnI₃ perovskite (green), and the oxidized sample upon exposure to air for 30 min (red).

To eliminate the possibility of frictional heat-induced reactivity during milling, several temperature-controlled experiments were performed. These include: 1) milling for 5 min, with 10 min cooling intervals (total milling duration remained at 60 min), with the temperature maintained around 27.5 °C, as monitored *via* an infrared thermometer; 2) milling at cryogenic temperatures using liquid N₂; and 3) heating of the solid mixture at 320 °C under Ar (Figures 2.19-2.21). The PXRD patterns of the interval milling and

cryomilling experiments matched with those of the desired cubic phase CsSnI_3 product (Figure 2.2). Conversely, thermal heating of the premixed solid precursors at 320 °C (the melting point of SnI_2) in a sealed flask under an inert Ar atmosphere resulted in the formation of the yellow orthorhombic phase, along with unreacted CsI. These results indicate that mechanochemical treatment is essential for the observed chemical reactivity, and product formation is not merely induced by frictional heat produced during milling. Subsequently, we verified the oxidation state of Sn in the mechanochemically synthesized CsSnI_3 perovskite with X-ray photoelectron spectroscopic (XPS) studies (Figure 2.2g). The measured binding energies of the $3d_{3/2}$ and $3d_{5/2}$ electrons suggested that the Sn existed as a single oxidation state species. Upon exposure to air for 30 min, an approximate 0.5 eV increase in the binding energies was observed, which corresponded to the formation of Sn(IV) due to oxidation. The ability to produce single-phase, air-sensitive Sn(II) perovskites, despite their innate susceptibility towards oxidation, illustrate the remarkable capability of our mechanochemical synthetic protocol in producing air-sensitive perovskite materials. In addition, the XPS survey spectra (Figures 2.11-2.15) showed no signals from any Fe species (Fe 3s and 3p electrons) that could have resulted from wear of the milling media *i.e.* the balls and the jar. This is important since metal contaminants from the milling media can affect the overall composition and property of the perovskite product.¹³¹

Besides X-ray diffraction and photoelectron spectroscopic characterization, scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) was employed (Figure 2.3) to confirm that the CsSnI_3 solid produced is a homogenous phase. The SEM studies revealed that the mechanochemically synthesized powder is composed of micron sized particles, and elemental mapping showed that it is indeed a homogenous phase (Figure 2.3a-d). Moreover, the elemental composition of the product by weight percentage

(wt %) and atomic percentage (atm %) derived from EDX corroborates with the CsSnI_3 perovskite formula (Figure 2.3e).

Figure 2.3. (a) SEM image of the mechanochemically synthesized CsSnI_3 perovskite, with the EDX analysis of the different elements (b) Cs (blue), (c) Sn (yellow), and (d) I (red), illustrating that the elements are homogeneously distributed throughout the solid particles. (e) The elemental composition as determined by EDX shows an approximately 1:1:3 molar ratio of Cs:Sn:I atoms, which coincides with the chemical formula of CsSnI_3 . The experimental weight percentages of each element showed no significant deviation from the calculated values.

The successful, efficient, and rapid formation of phase-pure CsSnI_3 encouraged us to expand our mechanochemical protocol to other halides precursors and obtain the corresponding CsSnX_3 ($\text{X} = \text{Cl}, \text{Br}$) perovskites. The desired perovskites were readily produced in their cubic phases, as evidenced by the PXRD data, without further optimization. The cubic polymorphs of the CsSnX_3 perovskites are all isostructural with only minor shifts in their relative peak positions of their PXRD patterns and can be readily distinguished from one another (Figure 2.4). For CsSnCl_3 to be isolated as the pure cubic phase is remarkable,

since the cubic polymorph is known to be a metastable high temperature phase and was previously thought to be achievable only by heating the monoclinic phase to elevated temperatures (117 °C).^{132,133} Furthermore, we investigated the formation of mixed halide perovskites such as $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ and $\text{CsSnBr}_{1.5}\text{I}_{1.5}$, which were readily obtained using our mechanochemical method. Notably, these mixed halide perovskite compounds are produced by using precise stoichiometric control, and they consist of phase-pure mixed halides rather than a mixture of their constituent single halide perovskites, as evidenced by PXRD analysis (Figure 2.4) and SEM-EDX studies (Figure 2.16). This highlights a major advantage of mechanochemistry over solution-based processes. For solution-based methods, the stoichiometric outcome of the product can depend on precursor solubility, temperature, and other reaction conditions, which can affect the recrystallization rates and thus the final composition of the material.⁸³ In addition, instances of solvent-free, neat, mechanochemical reactions facilitating the formation of cubic-phased compounds are rare.¹³⁴

The scalability of the mechanochemical solid-solid reaction was then investigated by the use of a planetary ball mill containing four 250 mL reaction vessels. We first attempted a 25 g (50 mmol scale) synthesis of CsSnBr_3 by neat milling CsBr and SnBr_2 for 3 h, using one 250 mL reaction vessel charged with a mixture of 4.0 g and 13.5 g stainless milling balls (BRR = 2.35). Remarkably, full conversion of the precursors occurred as confirmed by PXRD measurements (Figure 2.4). We isolated 23.55 g of the pure, black, cubic phase CsSnBr_3 perovskite product in the glovebox, which corresponded to a 94% yield. It is noteworthy that this scale-up from 200 mg in a shaker mill to 25 g in a planetary ball mill did not require much optimization, apart from increasing the reaction time and changing the BRR.

Figure 2.4. Comparison of the PXRD patterns of the mechanochemically synthesized: (a) 200 mg scale $\text{CsSnBr}_{1.5}\text{I}_{1.5}$, (b) 25 g scale CsSnBr_3 , (c) 250 g scale $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$, and (d) 200 mg scale $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$, (e) 200 mg scale CsSnCl_3 perovskites with the simulated (f) cubic and (g) monoclinic phases of CsSnCl_3 . The green dashed lines help to show that the various CsSnX_3 perovskites are distinct but isostructural to one another, and that they all correspond to the cubic polymorph. These scalable mechanochemical reactions clearly contain phase-pure cubic products. The (h) UV-vis DRS spectra and (i) PL spectra of the various mechanochemically synthesized perovskites. The PL of CsSnCl_3 perovskite was not detected.

Encouraged by these results, we then performed the mechanochemical synthesis of the mixed halide $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ perovskite on a 250 g scale, using the same 250 mL reaction vessel, as a proof-of-concept to access perovskites in “kg scales”. A powdered mixture of CsBr , CsCl , SnBr_2 , and SnCl_2 (0.29 mol each) was added to the reaction vessel in a N_2

glovebox and charged with a mixture of stainless balls (BRR = 1.30). The air-tight vessel was then installed in a planetary mill and the reagents were milled for a total of 10 h (see Supplementary Information for details). The milling time was increased to ensure that the reaction achieved completion. From this reaction, a bright orange solid powder (240.9 g, 96% isolated yield) was obtained (Figure 2.1c). Full utilization of all four vessel holders of the planetary mill would thus enable a solvent-free batch synthesis of around 1 kg of the desired perovskite. PXRD analysis of the product confirmed the absence of all the four precursors, and the pattern was indistinguishable from the pure, metastable cubic $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ (Figure 2.10). These large-scale experiments highlight the scalability of the mechanochemical reactions, without compromising the quality and selectivity of the products.

Subsequently, UV-visible diffuse reflectance spectroscopic (UV-vis DRS) and steady-state photoluminescence (PL) studies were conducted to evaluate the optical properties of our mechanochemically synthesized perovskites. The UV-vis spectra (Figure 2.4h) revealed that the tin halide perovskite absorb light within the 200-900 nm region, similar to their lead-based counterparts.⁸³ The powdered CsSnBr_3 and CsSnI_3 samples showed PL at 673 and 943 nm (Figure 2.4i) respectively, upon excitation using a 500 nm laser source, whereas their spin-coated thin film counterparts had very similar PL peaks positioned at 674 and 941 nm, respectively (Figure 2.18). These results suggest that the optical properties of the mechanochemically synthesized perovskite powders are essentially indistinguishable from the conventional solution processed thin film counterparts. For the mixed halide $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ and $\text{CsSnBr}_{1.5}\text{I}_{1.5}$, their UV-vis absorption maxima and PL positions are between those of their single halide counterparts, indicating the tunability of the optical properties for the mechanochemically synthesized perovskites. By simply varying the stoichiometric composition of each halide, it is possible to achieve

stoichiometrically altered perovskites with the specifically desired optical absorption, which is an accomplishment that is difficult for solution-based methods.

The ability to achieve the cubic phase for CsSnCl₃ perovskites by mechanochemistry inspired us to explore the possibility of obtaining the metastable high temperature phases for other perovskites. To establish that our ball milling methodology is applicable to all metal halide perovskites, we conducted the mechanochemical synthesis of the hybrid inorganic-organic FAPbI₃ (FA = formamidinium) perovskite and the pure inorganic CsPbI₃ perovskite systems. It is known that FAPbI₃ can exist as two polymorphs, namely the black trigonal and yellow hexagonal phases.¹³⁵ The metastable black trigonal phase of FAPbI₃ was previously obtained by heating the yellow hexagonal phase to 185 °C.¹³⁶ Similarly, for CsPbI₃, the metastable, non-nanocrystalline, black cubic phase was only achieved at elevated temperatures, up to 260 °C, as reported recently by Pradhan *et al.*¹³⁷ In addition, it is noteworthy that such solution processing methods had either been unsuccessful in obtaining a pure high temperature phase product for these two lead-based perovskites at room temperature, or required the use of corrosive starting reagents like hydroiodic acid or sustained heating for several days.

For the mechanochemical synthesis of FAPbI₃, our preliminary reaction involved ball milling FAI and PbI₂ in a shaker mill for 1 h. Despite the product having a black powder-like consistency, PXRD analysis revealed that it composed of a mixture of the yellow hexagonal and black trigonal phases, consistent with solution-based results.¹³⁶ In order to obtain a pure-phase product, the mechanochemical reaction conditions had to be optimized. It had been previously established that mechanochemistry can be used to alter product selectivity⁸⁰ by changing certain experimental perimeters such as the milling frequency, duration of milling, or the BRR. Such solid-state selectivity can also be enhanced

by the addition of small quantities of a liquid additive, which serves as a lubricant to improve mixing of the reagents, a technique known as liquid-assisted grinding (LAG).¹³⁸ Systematic screening of all these parameters (Figure 2.5a) revealed that the pure yellow hexagonal phase can be readily obtained by solvent-free milling for 10 min, while the pure black trigonal phase can be afforded by LAG for 15 min, using pentane as the liquid additive. Prolonged milling led to the formation of mixed phase products. It is significant that our mechanochemical protocol enabled selective access to the metastable FAPbI₃ at room temperature without further annealing. The rapid (10-15 min) and efficient formation of the pure individual phases by mechanochemistry further highlights its benefits over the solution-based counterparts. The UV-vis DRS spectrum of the FAPbI₃ indicated that the absorption edge is at 800 nm, with the PL maximum at 814 nm (Figure 2.5b), which are consistent with the reported values.¹³⁶ The time-resolved PL (TRPL) measurement of the as-synthesized trigonal phase powder was also conducted at 130 $\mu\text{J cm}^{-2}$ and two decay processes were observed. The fast decay process with a 270 ps life-time (69%) is likely to be related to the trap-assisted recombination whereas the slow process with 1.6 ns (31%) could originate from free charge-carrier recombination (Figure 2.5c).

Figure 2.5. (a) The PXRD patterns for the mechanochemically synthesized FAPbI₃ perovskites at different conditions. (b) UV-vis DRS and PL measurements of the trigonal FAPbI₃ synthesized using our solvent-free protocol. (c) TRPL of as-synthesized trigonal FAPbI₃ upon excitation at 400 nm. The plot was fitted biexponentially to give a short-lived process with a lifetime of 270 ps, and a longer process with a lifetime of 1.6 ns.

Likewise, for the synthesis of the all-inorganic CsPbI₃ perovskite, our mechanochemical protocol involved ball milling of CsI and PbI₂ precursors for 15 min, which rapidly afforded the desired high temperature black cubic phase, as confirmed by PXRD (Figure 2.17a). This is notably contrary to reported solution-based protocol, which utilizes corrosive hydroiodic acids, requires additional capping reagents such as oleic acids and oleylamine, as well as molten Cs-oleate precursors.¹³⁷ *Ex situ* PXRD measurements revealed that ball milling for only 5 min resulted in the formation of a mixed black cubic

and yellow orthorhombic phase product. The yellow orthorhombic phase then rapidly converts into the black cubic phase upon prolonged milling. The UV-vis absorption edge of the synthesized powder product was determined to be at 700 nm while the PL maximum was centered at 724 nm (Figure 2.17b). TRPL measurements were also carried out at $20 \mu\text{J cm}^{-2}$ and revealed two decay processes with lifetimes of 85 ps and 1.1 ns (Figure 2.17c).

2.2.2 Solvent-free fabrication of functional devices

To date, perovskites have been widely studied for their optoelectronic properties. Despite numerous reports of lead halide perovskites for optoelectronic applications, their tin-based counterparts are plagued by undesirable dark conductivity at room temperature due to high densities of defects, so their incorporation into devices remains challenging. Yet, it has been previously proposed that the orthorhombic black CsSnI_3 can be used as a promising alternative to toxic gallium arsenide (GaAs) as a semiconductor material.^{40,139} In addition, the cubic CsSnBr_3 has also shown great potential for photodetector applications.¹³⁰

To demonstrate that functional devices can be made from their precursors in a completely solvent-independent manner, we fabricated photodetector devices without the use of any solvents by utilizing our mechanosynthesized perovskites and evaluated their performances by conducting photocurrent measurements. The devices can be readily made by mechanically compressing the perovskite powders into small discs using a hydraulic pelleting press under an inert N_2 atmosphere. Subsequently, gold electrodes were then vapor deposited onto the disks to create an active device area of $8.0 \times 10^{-3} \text{ cm}^2$ (Figure 2.6a). The photocurrent measurements of the devices were then conducted under the illumination of a 445 nm LED lamp under vacuum. Among the examined tin-based devices, $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ was found to perform the best (Figure 2.6b) which exhibited nearly ten times as much

current (44.3 nA) under illumination than in the dark (4.94 nA). The device also displayed on-off responsiveness without significant hysteresis during the working cycles (Figure 2.6b), with an overall responsivity and detectivity of 0.081 mA/W and 1.8×10^{-8} Jones respectively. Nevertheless, due to the limitations of the instrumental setups, short-term exposure of these devices to air for several seconds was inevitable, which could cause Sn(II) oxidation on the exposed top surfaces. Such small amounts of Sn(IV), which would be detected by XPS experiments, were likely to be the cause of the high dark current that we detected. However, it is interesting to note that these tin-based perovskite device performance data have not been determined or reported previously. On the contrary, we were not able to conclusively evaluate the solution-processed thin film devices made by spin-coating due to the poor solubility of the perovskite powders as well as their precursor salts. Furthermore, the solution-based processing method was further compounded by problems such as reproducibility, oxidation, and phase impurities of the thin films. These problems had been previously well-documented for all-inorganic and hybrid inorganic-organic tin-based perovskites,¹⁴⁰ since they directly affect the optoelectronic properties of the devices and thus impede their widespread applicability. Again, we must reiterate that devices (film or disk) made from pure inorganic tin-based mixed halide perovskites of the type $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ had not been reported before. Through simple utilization of a hydraulic press, we were able to fabricate a prototype device using our mechanochemically synthesized $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ powders, which could be obtained in multigram to kilogram scales. The employment of mechanochemical ball milling combined with the use of a hydraulic press represents the pioneering synthetic protocol to fabricate a functional device from bulk precursors in a completely solvent-free and feasibly scalable manner.

Figure 2.6. (a) Images of the fabricated photovoltaic device made from mechanochemically synthesized $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$. (b) The current vs. time curve for a device made from mechanochemically synthesized $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ with a light intensity of 0.55 mW under a bias of 0.10 V, denoting multiple light-dark cycles.

Zhou et al. prepared an all-inorganic perovskite-based MSM photodetector with a bilayer composite film of mesoporous TiO_2 and CsPbBr_3 quantum dots, where the responsivity reached $\sim 3500 \text{ mA}\cdot\text{W}^{-1}$, with about 44 times increase compared to that of a pure CsPbBr_3 device ($\sim 80 \text{ mA}\cdot\text{W}^{-1}$).¹⁴¹ When it is pure CsPbBr_3 (MSM-II), the performance is rather poor with the responsivity at $\sim 80 \text{ mA}\cdot\text{W}^{-1}$. They claim this is due to the lack of connection between QDs which exists in the MSM-I owing to the scaffold of TiO_2 . And this might be the same reason that our devices show poor performance. The voids in the palettes is detrimental to the charge transfer. But TiO_2 only gives a limited performance boost, thus it will not be an ultimate solution. Meanwhile, as the best Sn-based photodetector, MASnI_3 NWs based devices were found to be functional with a $1.1 \text{ mW}\cdot\text{cm}^2$ intensity, and the responsivity could reach up to $0.47 \text{ A}\cdot\text{W}^{-1}$ with specific detectivity of 8.80×10^{10} Jones. This high detectivity value is comparable to other lead perovskite-based photodetectors.¹⁴²

Compared to these reported results, the $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ based devices still have plenty of room to improve. It is speculated that the intrinsic feature of the mechanochemical method limits the crystallinity of the powder product, which consequently affects the overall performance of the photodetector devices. Additionally, the proposed dry method for device fabrication is determined to be too rough to produce any smooth surface out of large and non-uniform particles. Therefore, the photo-generated charge carriers suffer from poor conductivity across the device surface to reach the electrodes.

2.3 Conclusions

In summary, we have developed a mechanochemical protocol for the rapid, solvent-free, general synthesis of multiple metal halide perovskites, which can be produced up to kilogram scales. Several metastable phases for the various perovskites can also be achieved mechanochemically in high purity, while circumventing the need for post-synthetic thermal treatment. Moreover, we established a completely solvent-free protocol to fabricate a photodetector device from these powders *via* a hydraulic press, creating the first functional device based on $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ perovskite. These results highlight the prominent advantages of our mechanochemical approach for the synthesis of perovskites and underscore the promise of mechanochemistry for the solvent-free, large-scale fabrication of perovskite devices. We believe that our solvent-free mechanochemical methodology can dramatically reduce the energetic and environmental footprint for the synthesis of perovskites and fabrication of devices, thus pave the way for broader adoption by industry in the future.

2.4 Materials, instrumental details and synthetic methods

Cesium chloride (99%), cesium bromide (99.99%), cesium iodide (99.99%), lead iodide (99.999%) and formamidinium iodide (FAI, >99% anhydrous) were purchased from Sigma-Aldrich. Tin(II) chloride (99%) was purchased from Alfa Aesar. Tin(II) bromide (99.9%) was purchased from Sigma-Aldrich and tin(II) iodide (99.99%) was purchased from Strem Chemicals Corp. All the above chemicals were used directly without further purification and stored in a glovebox to minimize the exposure to oxygen. Anhydrous dimethyl sulfoxide (DMSO, >99.9%) was purchased from Sigma-Aldrich and stored in a glovebox.

Fabrication of devices for photocurrent measurements. The perovskite powder sample (300 mg) was placed between two stainless steel pellets in a hydraulic press and compressed with a force of 10^4 kg for 15 m.

Powder X-ray diffraction study. Measurements were performed on a Rigaku SmartLab X-ray diffractometer, fitted with a copper ($K_{\alpha 1}$ (1.54059)/ $K_{\alpha 2}$ (1.54441) = 2) target X-ray tube set to 40 kV and 30 mA and a SC-70 scintillation detector. A medium resolution parallel-beam (PB) cross beam optics (CBO) unit was used with a 10 mm slit width. The powder samples were packed in airtight specimen holders (Bruker A100B33) in a glovebox. The respective PXRD patterns were obtained for 2θ angles from 4° to 50° at 0.04° per step.

Ultraviolet-visible diffuse reflectance spectroscopic (UV-vis DRS) study. UV-vis spectra were acquired using a Shimadzu UV-3600 UV-vis spectrometer with an integrating sphere (Shimadzu ISR-3100). Powder samples were sealed in quartz cuvettes.

X-ray photoelectron spectroscopic study. Samples were prepared by coating a uniform layer of the materials on SPI double-sided adhesive carbon tape in a glovebox. The carbon tape contains acrylate adhesives, so both C 1s and O 1s signals are present in the carbon

tape itself. The XPS data were processed using the CasaXPS software. The spectra were calibrated internally according to the adventitious C 1s position at 284.6 eV.

Photoluminescence spectroscopic study. Measurements were carried out and ultrafast femtosecond optical spectroscopic methods were employed to measure the PL data and FWHM of the thin films. A Coherent Libra regenerative amplifier (50 fs, 1 kHz, 800 nm) seeded by a Coherent Vitesse Oscillator (100 fs, 80 MHz) were used as the pump laser sources. For pump wavelength tuning, the Coherent OPerA Solo optical parametric amplifier was used. Upon optically pumping the samples, the respective PL emissions were collected at a backscattering angle of 150° by a collimating lens pair and guided into an optical fiber that was coupled to a spectrometer (Acton, SpectraPro 2500i and SP2300) and detected by a charge coupled device (CCD; Princeton Instruments, Pixis 400B). Time-resolved PL (TRPL) was collected using an Optronis Optoscope streak camera system. Due to the moisture sensitivity of the perovskites prepared, all samples were contained inside air-tight encapsulations. The optical measurements were performed at room temperature under ambient conditions. The fitting was done according to the following equation:

$$y = y_0 + A_1 * \exp\left(-\frac{x-x_0}{t_1}\right) * \left(1 - \operatorname{erf}\left(-\frac{x-x_0-\frac{s^2}{t_1}}{s}\right)\right) + A_2 * \exp\left(-\frac{x-x_0}{t_2}\right) * \left(1 - \operatorname{erf}\left(-\frac{x-x_0-\frac{s^2}{t_2}}{s}\right)\right)$$

with x_0 and y_0 as the intercept on the axes, A as the amplitude of each component, s as the response time, erf as the error function, t_1 and t_2 as the lifetimes derived from the fitting results.

Photoelectrical study. Photoelectrical measurements were carried out using a Keithley 4200-SCS semiconductor characterization system with a coupled light source (Thorlabs

Solis-445C) and a DC2200 driver. For each as-prepared perovskite pellet, 200 nm thick gold electrodes were deposited through thermal evaporation using shadow masks (4000 $\mu\text{m} \times 200 \mu\text{m}$). Detectivity is calculated using the formula below:

$$\text{Detectivity} = \text{Responsivity} \times \sqrt{\frac{\text{Device area}}{2e \times I_{\text{dark}}}}$$

Fabrication of solution processed samples

General procedure for the fabrication of a thin film sample: 10 μL of a 0.40 M precursor solution in DMSO was spin coated onto a quartz substrate at 4000 rpm for 30 s. In order to obtain high quality films, 100 μL of toluene were dropped onto the substrate spinning at 4000 rpm for another 30 s. The coated substrate was then placed on a hot plate at 90 $^{\circ}\text{C}$ for 10 min.

Control experiments with heating only under solvent-free conditions

Stoichiometric equivalents of the precursors were mixed and sealed in a 25 mL reaction tube, heated at 325 $^{\circ}\text{C}$ under an argon atmosphere, cooled down to room temperature, and transferred into a glovebox. The reaction tube was unsealed and the resulting solid mixture was characterized by PXRD.

Fabrication of devices for photocurrent measurements

The perovskite powder sample (300 mg) was placed between two stainless steel pellets in a hydraulic press and compressed with a force of 10^4 kg for 15 min. One of the resultant sample discs is shown in Figure 2.5(a).

Mechanochemical syntheses

General procedure for mechanochemical synthesis: Stoichiometric equivalents of precursors (1:1 ratio between cation A^+ and B^{2+}) were mixed in a 25 mL stainless-steel

Form-Tech Scientific smart-snap milling jar equipped with a stainless-steel milling ball in a glovebox. The milling jar was installed into a Retsch MM400 shaker mill and the milling was operated at a frequency of 30 Hz for 1 h. The milling jar was then taken into a glovebox, unsealed, and the resulting product was collected.

Figure 2.7. Photographs of the mechanochemical synthesis of CsSnBr_3 as an example (a) before and (b) after ball milling; (c) milling jars were sealed with paraffin film and electrical tape to prevent exposure to air.

CsSnI₃: The general procedure was used with the following quantities: cesium iodide (77.9 mg, 0.30 mmol) and tin(II) iodide (112 mg, 0.30 mmol). The resulting product (150 mg, 79% yield) was collected as a black powder.

CsSnBr₃: The general procedure was used with the following quantities: cesium bromide (106 mg, 0.50 mmol) and tin(II) bromide (139 mg, 0.50 mmol). The resulting product (225 mg, 92% yield) was collected as a black powder.

CsSnCl₃: The general procedure was used with the following quantities: cesium chloride (84.2 mg, 0.50 mmol) and tin(II) chloride (94.8 mg, 0.50 mmol). The resulting product (145 mg, 81% yield) was collected as a yellow powder.

CsSnBr_{1.5}Cl_{1.5}: The general procedure was used with the following quantities: cesium bromide (53 mg, 0.25 mmol), tin(II) bromide (70 mg, 0.25 mmol), cesium chloride (42 mg,

0.25 mmol), and tin(II) chloride (47 mg, 0.25 mmol). The resulting product (169 mg, 79% yield) was collected as an orange powder.

CsSnBr_{1.5}I_{1.5}: The general procedure was used with the following quantities: cesium iodide (65 mg, 0.25 mmol), tin(II) iodide (93 mg, 0.25 mmol), cesium bromide (53 mg, 0.25 mmol), and tin(II) bromide (70 mg, 0.25 mmol). The resulting product (228 mg, 81% yield) was collected as a black powder.

CsPbI₃: The general procedure was used with the following quantities: cesium iodide (130 mg, 0.50 mmol) and lead(II) iodide (230 mg, 0.50 mmol). The mixed powder was ball-milled for 15 min resulting in the product (295 mg, 82% yield) as a black powder.

FAPbI₃: The general procedure was used with the following quantities: FAI (57 mg, 0.33 mmol), lead(II) iodide (153 mg, 0.33 mmol), and 0.10 mL of pentane added to assist the ball-milling (liquid assisted grinding, LAG). The mixture was milled for 15 min and the resulting product (168 mg, 80% yield) was collected as a black powder.

Table 2.1. Synthetic details of the mechanochemically synthesized CsSnX₃ (mg scale).

ABX₃	Quantity of precursors	Product appearance	Yield
CsSnI ₃	CsI (77.9 mg, 0.30 mmol)	black powder	150 mg,
	SnI ₂ (112 mg, 0.30 mmol)		79%
CsSnBr ₃	CsBr (106 mg, 0.50 mmol)	black powder	225 mg,
	SnBr ₂ (139 mg, 0.50 mmol)		92%
CsSnCl ₃	CsCl (84.2 mg, 0.50 mmol)	yellow powder	145 mg,
	SnCl ₂ (94.8 mg, 0.50 mmol)		81%
CsSnBr _{1.5} Cl _{1.5}	CsBr (53 mg, 0.25 mmol)	orange powder	169 mg,
	SnBr ₂ (70 mg, 0.25 mmol)		
	CsCl (42 mg, 0.25 mmol)		
	SnCl ₂ (47 mg, 0.25 mmol)		

CsSnBr _{1.5} I _{1.5}	CsI (65 mg, 0.25 mmol)	black powder	228 mg, 81%
	SnI ₂ (93 mg, 0.25 mmol)		
	CsBr (53 mg, 0.25 mmol)		
	SnBr ₂ (70 mg, 0.25 mmol)		
CsPbI ₃	CsI (130 mg, 0.50 mmol)	black powder	295 mg, 82%
	PbI ₂ (230 mg, 0.50 mmol)		
FAPbI ₃	FAI (57 mg, 0.33 mmol)	black powder	168 mg, 80%
	PbI ₂ (153 mg, 0.33 mmol)		
	0.10 mL pentane for LAG		

Large-scale synthesis:

CsSnBr₃ (25 g scale): Cesium bromide (10.6 g, 50 mmol) and tin(II) bromide (13.9 g, 50 mmol) were mixed in a 250 mL stainless-steel milling jar equipped with eight 4.0 g and fifteen 13.5 g stainless-steel milling balls (ball to reactant ratio = 2.35) in a glovebox. The milling jar was then installed into a Grinder BM4 planetary mill with four vessel holders and the milling was operated at 300 revolutions per minute (rpm, sun wheel speed) for cycles consisting of 3 min of continuous milling and a pause for 1 min, followed by a reverse in the rotation direction after each cycle, for a 3 h total milling duration. The milling jar was then taken into a glovebox, unsealed, and the resulting black product (23.6 g, 94% yield) was collected.

Figure 2.8. Photographs of the large-scale (25 g) synthesis of CsSnBr_3 (a) before and (b) after ball milling.

$\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ (250 g scale): Cesium bromide (62.6 g, 0.29 mol), cesium chloride (49.6 g, 0.29 mol), tin(II) bromide (81.9 g, 0.29 mol), and tin(II) chloride (55.8 g, 0.29 mol) were mixed in a 250 mL stainless-steel milling jar equipped with fourteen 4.0 g and twenty 13.5 g stainless-steel balls (ball to reactant ratio = 1.30) in a glovebox. The milling jar was then installed into the same planetary mill and operated with the same milling cycles as the 25 g scale above, for a $2+2+2+2+2 = 10$ h total milling duration. Such interval milling was performed to prevent overheating and reduce wear and tear on the planetary mill. The milling jar was then taken into a glovebox, unsealed, and the resulting black product (241 g, 96% yield) was collected.

Figure 2.9. Photographic demonstration of the kg-scale synthesis of $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$. a) Preparation of the reagents CsBr , CsCl , SnBr_2 , and SnCl_2 (all white powders) in a N_2

glovebox. The reagents were weighed and transferred from a beaker into the 250 mL mechanochemical reaction vessel. The total reagent weight was 250 g. b) The reagent mixture with the milling balls at the bottom of the vessel. c) Gentle mixing of the reagents, which exposed the milling balls, by using a metal spatula. d) Planetary mill containing four reaction vessel holders, essentially allowing four 250 g reactions to take place simultaneously, leading to a 1.0 kg scale batch synthesis of the perovskite. e) The orange product after 10 h of milling.

2.5 Supplementary characterization data

The perovskite material $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ have been successfully synthesized from milligram scale to kg-scale. To validate this scalability, PXRD studies was conducted to investigate the purity of the observed products as shown in Figure 2.10. The product produced in 250 g scale did not show any significant deviation compared to the product in 200 mg scale in terms of the PXRD patterns.

Figure 2.10. Comparison of the PXRD patterns of CsSnBr_{1.5}Cl_{1.5} perovskite synthesized in 200 mg and 250 g scales, and the CsBr, CsCl, SnBr₂, and SnCl₂ precursors. The PXRD pattern of the 250 g scale synthesized product is almost indistinguishable from the small scale one and does not contain any precursor peaks.

XPS experiments and data

Sn-based perovskite materials are known for their instability in air due to the rapid oxidation of tin(II) to tin(IV). Hence, it is crucial to determine the oxidation state of Sn after the synthesis and XPS studies were conducted to acquire the valid information. The XPS experiments were also performed for the oxidized samples for comparison. These results clearly show the intact tin(II) species in our freshly prepared products. Moreover, these results demonstrated the capability of our mechanochemical method to handle air-sensitive materials and synthesis.

Figure 2.11. (a) Sn 3d XPS data for CsSnI₃. (b) Survey spectrum of CsSnI₃. (c) Sn 3d XPS data in CsSnI₃ after being exposed to air.

Figure 2.12. (a) Sn 3d XPS data for CsSnBr₃. (b) Survey spectrum of CsSnBr₃. (c) Sn 3d XPS data in CsSnBr₃ after being exposed to air.

Figure 2.13. (a) Sn 3d XPS data for CsSnCl₃. (b) Survey spectrum of CsSnCl₃. (c) Sn 3d XPS data in CsSnCl₃ after being exposed to air.

Figure 2.14. (a) Sn 3d XPS data for CsSnBr_{1.5}I_{1.5}. (b) Survey spectrum of CsSnBr_{1.5}I_{1.5}. (c) Sn 3d XPS data in CsSnBr_{1.5}I_{1.5} after being exposed to air.

Figure 2.15. (a) Sn 3d XPS data for CsSnBr_{1.5}Cl_{1.5}. (b) Survey spectrum of CsSnBr_{1.5}Cl_{1.5}. (c) Sn 3d XPS data in CsSnBr_{1.5}Cl_{1.5} after being exposed to air.

Besides XPS characterization, SEM-EDX was employed to confirm that the CsSnBr_{1.5}Cl_{1.5} solid produced is a homogenous phase. As shown in Figure 2.16 b, the mechanochemically synthesized powder was found to be micron-size and the elemental mapping showed that it is indeed a homogenous phase with high purity. Moreover, the elemental composition of the product by weight percentage (wt %) and atomic percentage (atm %) derived from EDX corroborates with the CsSnBr_{1.5}Cl_{1.5} perovskite formula.

Figure 2.16. (a) SEM image of the mechanochemically synthesized $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$ perovskite, with the EDX analysis of the different elements (b) Cs (blue), (c) Sn (red), (d) Br (yellow), and (e) Cl (green), illustrating that all the elements are homogeneously distributed throughout the solid particles. (f) The elemental composition as determined by EDX shows an approximately 1:1:1.5:1.5 molar ratio of Cs:Sn:Br:Cl atoms, which coincides with the chemical formula of $\text{CsSnBr}_{1.5}\text{Cl}_{1.5}$. It is worth noting that such precise stoichiometry is hard to achieve by solution-based methods.

PXRD and photoluminescence studies of CsPbI₃

The synthesis of the all-inorganic CsPbI₃ perovskite using our mechanochemical protocol involved ball milling of CsI and PbI₂ precursors for 15 min, which rapidly afforded the desired high temperature black cubic phase, as confirmed by PXRD (Figure 2.17a). *Ex situ* PXRD measurements revealed that ball milling for only 5 min resulted in the formation of a mixed black cubic and yellow orthorhombic phase product. The yellow orthorhombic phase then rapidly converts into the black cubic phase upon prolonged milling. The UV-vis absorption edge of the synthesized powder product was determined to be at 700 nm while the PL maximum was centered at 724 nm (Figure 2.17b). TRPL measurements were also carried out at 20 $\mu\text{J cm}^{-2}$ and revealed two decay processes with lifetimes of 85 ps and 1.1 ns (Figure 2.17c).

Figure 2.17. (a) The PXRD patterns of CsPbI₃ synthesized with different reaction durations and the simulated patterns for cubic and orthorhombic phases. (b) The UV-vis DRS spectrum (black) and the steady-state PL (red) of CsPbI₃. (c) The TRPL spectrum (black)

of CsPbI_3 . The plot was fitted biexponentially (red) to give a short-lived process with a lifetime of 85 ps (69%) and a longer process with a lifetime of 1.1 ns (31%).

The fabrication of thin film samples was also attempted by using solutions of the perovskite precursors. However, the consistency and quality of these samples varied dramatically, especially for the mixed halide samples. We speculated that the differences of solubility of the precursors played an important role determining the crystallization and film formations. The PL studies of these thin film products were conducted, and the results are shown in Figure 2.18. Nevertheless, further optimization of the fabrication must be done to improve the reliability and reproducibility of the data.

Figure 2.18. PL data of spin-coated films of CsSnBr_3 (blue), $\text{CsSnBr}_{1.5}\text{I}_{1.5}$ (green), and CsSnI_3 (red).

PXRD studies of control experiments

A series of control reactions were carried out to test the validity of mechanochemistry for the syntheses of perovskites. A cryomilling experiment was carried out to rule out the heating effect during the reactions (Figure 2.19). We also monitored and controlled the

reaction temperature (Figure 2.20) during the mechanochemical synthesis which helped us to conclude that the heat generated by milling is not an effective energy source for the reaction to occur.

A heating control experiment was performed by heating the solid mixture of the precursors up to the melting point for the same duration of reaction time. This only resulted in a undesirable mixture of solid products including the precursors and the yellow orthorhombic phase of CsSnI_3 , as shown in Figure 2.21c.

Figure 2.19. Photographs and data of the cryomilling synthesis of CsSnI_3 . (a) Photograph of cryomilling setup with liquid N_2 flow. (b) Photograph showing the black perovskite phase product obtained by cryomilling. (c) PXRD pattern of the product from cryomilling, showing a pure orthorhombic (black) phase.

Figure 2.20. Controlled-temperature mechanochemical synthesis of CsSnI_3 . (a) Reaction temperature monitored over 1 h during a milling experiment. The milling jars were then

allowed to cool down to below 28 °C every 5 min before the milling resumed. (b) Photograph of a reaction monitored by an IR thermometer. (c) PXRD pattern of the product showing a pure orthorhombic (black) phase.

Figure 2.21. Control experiments for the attempted synthesis of CsSnI_3 perovskite with heat only under solvent-free conditions. (a) Photograph of the solid reaction mixture being heated in a sand-bath equipped with a temperature sensor. (b) Photograph of the resulting product after heating to 320 °C for 1 h, showing a multi-colored solid. (c) Comparison of the PXRD patterns of the perovskite powder that was synthesized mechanochemically (red line) and the heated solid product (black line). Multiple compounds can be identified from the thermal reaction, including SnI_2 and CsSnI_3 in the yellow orthorhombic phase as the major components.

The thin film samples on the other hand did not share the same high purity or reproducibility of the mechanochemically synthesized products based on the result of PXRD as shown in Figure 2.22.

Figure 2.22. Comparison of the PXRD patterns of the CsSnI_3 perovskite that was synthesized mechanochemically (red line), with the sample prepared in solution by heating and spin-coating a thin film onto a glass substrate (black line). The product obtained by solution processing is not pure, since characteristic peaks belonging to the black orthorhombic phase and several other unidentifiable peaks were observed.

The fabrication of the photoelectrical devices required several steps involving different instruments. It is inevitable to transfer these materials between different locations, *i.e.* from one glovebox to another, and the minimal exposure during these transits must be considered. Therefore, PXRD experiments were also conducted for the fabricated devices to confirm that these samples remained in pristine conditions. As shown in Figure 2.23, no significant structural change was observed when the device was compared to the freshly prepared materials before the fabrication of devices. We believe that the results of the photoelectrical measurements are reliable and reproducible.

Figure 2.23. Comparison of the PXRD patterns of the CsSnBr_{1.5}Cl_{1.5} perovskite device after gold electrode deposition with the as-synthesized powder. The peak position at 24° corresponds to the paraffin film that was used to seal the device in order to prevent the exposure to air. Based on the PXRD analysis, there is no significant structural change in the CsSnBr_{1.5}Cl_{1.5} perovskite before and after the process of device fabrication.

Chapter III

Understanding the Origins of Nucleophilic Hydride Reactivity of Sodium Hydride-Iodide Composite

*This chapter is adapted from a published work (Chem. Eur. J. **2016**, 22, 7108 – 7114). The authors include Zonghan Hong, Derek Yiren Ong, Subas Kumar Muduli, Pei Chui Too, Guo Hao Chan, Ya Lin Tnay, Shunsuke Chiba, Yusuke Nishiyama, Hajime Hirao, and Han Sen Soo. The author of this thesis contributed in the major part of this work including experiments and analysis of PXRD, XPS, ssNMR. The DFT study was done by Dr. Hajime Hirao.*

ABSTRACT: As a common main group compound, sodium hydride (NaH) has been commonly used as a Brønsted base in chemical syntheses, while it has rarely been employed to add hydride (H[−]) to unsaturated electrophiles. In this chapter, mixing NaH with NaI or LiI in tetrahydrofuran (THF) as a solvent was found to provide a new inorganic composite, NaH-NaI, which can effect even stereoselective nucleophilic hydride reductions of nitriles, imines, and carbonyl compounds. The composite consists of NaI interspersed with activated NaH, as revealed by powder X-ray diffraction, and both solid-state nuclear magnetic resonance and X-ray photoelectron spectroscopy. DFT calculations implicate that this remarkably simple inorganic composite, which is comprised of NaH and NaI, gains nucleophilic hydridic character similar to covalent hydrides, resulting in unprecedented and unique hydride donor chemical reactivity.

3.1 Introduction

Main group materials and compounds are getting more favored in the context of green chemistry, regardless that transition metals are still dominating the field of catalysis. Among all the main group materials, hydride compounds are commonly used for various applications, from CaH_2 as a typical desiccant to palladium hydride being charged in hydrogen fuel-cell automobiles. Mostly, hydrides are treated as strong bases and reducing agents in synthesis, such as NaH and NaBH_4 respectively. Sodium hydride (NaH) is one of the simplest earth-alkaline metal ionic hydride compounds with a cubic halite crystal structure. Similar to other alkali metal hydrides that consist of M^+ (M = alkali metal) and H^- ions bound together strongly via electrostatic attraction, NaH is practically insoluble in organic solvents and reacts with protic solvents.⁹⁴⁻⁹⁶ Consequently, the reactivity of NaH was previously thought to be limited exclusively to Brønsted basic or single electron transfer (SET) activity,⁹⁴⁻⁹⁶ and has rarely been invoked as a two-electron hydride (H^-) transfer agent.⁹⁷⁻¹⁰² Instead, a number of covalent hydrides, including boranes, silanes, metal borohydrides, and metal aluminum hydrides have typically been utilized as the reagents of choice in nucleophilic H^- transfer reactions.^{143,144}

A remarkable and unprecedented decyanation reaction enabled by NaH in the presence of iodide additives was rediscovered recently (Scheme 3.1).¹⁰³⁻¹⁰⁶ Sodium iodide (NaI), lithium iodide (LiI), and magnesium iodide (MgI_2) were identified as suitable additives for mediating this unusual reaction, implicating the critical role of dissolved iodide in the mixture.¹⁰³ The substrate scope is broad and the stereo-configuration during the nitrile substitution with hydride was retained (Scheme 3.1).¹⁰³ We have expanded the substrate scope to include other unsaturated compounds such as amides, imines esters, and carbonyl compounds.¹⁰³

(a) Reductive decyanation

(b) Reduction of Amide

(c) Reduction of imine

Scheme 3.1. (a) Nucleophilic hydride substitution of nitrile with retention of stereo-configuration; (b) reduction of amides; and (c) reduction of imines.

Through a series of kinetics experiments and substrate screening, we proposed that NaH and the dissolved I^- ions recrystallized as smaller fragments of a NaH-NaI composite.¹⁰³ This composite possesses nucleophilic hydride transfer reactivity, which can potentially be employed in the reduction of numerous unsaturated substrates such as carbonitriles, imines, and carbonyl compounds.^{97-102,143-145} Given the extensive applicability of this new material, and the plausible use of I^- to activate other simple ionic materials for novel organic transformations, our team has conducted a series of characterization experiments on this NaH-NaI composite. Herein, we present evidence to establish the interfacial interactions between NaH and NaI, which supports our previous experimental and DFT work that the NaH-NaI composite consists of smaller, activated fragments of NaH.

3.2 Materials Characterization of NaH-LiI and NaH-NaI Composites

In our reactivity and kinetics studies, the decyanation reactions by NaH-LiI and NaH-NaI exhibited an induction period of at least 0.5 h, independent of the substrates. Indeed, the NaH-Na(Li)I composite materials isolated after the thermal treatment in THF could initiate the decyanation reactions without the induction period. These observations suggest that the reaction of NaH with LiI (or NaI) resulted in the formation of new inorganic composite materials that display the remarkable hydride transfer reactivity. Thus, we subjected these composites to a suite of spectroscopic and structural analyses to elucidate the origin of the observed reactivity: powder X-ray diffraction (PXRD), FTIR spectroscopy, and solid-state NMR spectroscopy provided information about the bulk composition, whereas X-ray photoelectron spectroscopy (XPS) to investigate the surface properties confirmed our previous DFT studies.

The PXRD patterns of the NaI and LiI composites unambiguously demonstrated that in the bulk composition for both of the materials, the same cubic NaI crystal phase was present in crystalline form, and there was remarkably no trace of LiI (Figure 3.1).¹⁴⁶⁻¹⁴⁸ Appreciable amounts of NaH were observed in both of the samples prepared from NaI or LiI, which confirmed that the NaH coexists with the NaI crystal phase.¹⁴⁹ No peaks corresponding to NaOH or LiOH were observed, indicating that the composites did not contain crystalline components of both hydroxides. Rietveld refinement performed on the PXRD data suggested that the NaH-LiI sample had a composition of $\text{NaI}_{0.73}\text{H}_{0.27}$ (Figure 3.1a) whereas the NaH-NaI composite had a composition of $\text{NaI}_{0.63}\text{H}_{0.37}$ (Figure 3.1b).^{148,149} After using the NaH-NaI composite for the decyanation, the composition was converted into $\text{NaI}_{0.81}\text{H}_{0.19}$ (see Figure 3.2a and Table 3.1). The PXRD studies provide evidence that LiI had dissolved and recrystallized as NaI through solvothermal salt metathesis,^{150,151} and some crystalline domains of NaH remained in the bulk composition of both samples.

Figure 3.1. PXRD study for (a) the NaH-LiI sample, and (b) the NaH-NaI sample. The experimental data (black) and the Rietveld refinements (red) are compared to the components of NaI (green) and NaH (blue).

To probe the surface content of the composite materials, XPS was conducted on the composites (Figures 3.3 and 3.4) as well as pristine samples of NaH, NaI, and LiI (Figures 3.12-3.14 respectively, and Table 4.2). All the XPS data have been calibrated internally to the C 1s signal from the carbon tape used. Remarkably, for the NaH-LiI composite, a minor component (26%) is observed at 1072.0 eV (Figure 3.3a), which does not correspond to the Na 1s peaks of pristine NaH or NaI (Figure 3.12a and 3.13a, respectively) that coincide around 1070 eV.^{152,153} Likewise, for the NaH-NaI composite, a new appreciable component

(44%) is detected at 1072.4 eV (green line, Figure 3.4a), which is distinct from the Na 1s signals at 1069.8 eV for NaH and NaI (Figure 3.12a and 3.13a, respectively).

Figure 3.2. (a) PXRd data for the NaH-NaI composite after reduction reaction (black). The Rietveld refinement (red) is compared to the components NaI (green) and NaH (blue). Two unidentified peaks at $2\theta = 34.4^\circ$ and 38.1° (marked with *), which cannot be attributed to NaCN, NaNH₂, or NaOH, were found. (b) Na 1s XPS data for the NaH-NaI composite after reduction reaction (black) with the fit (red) and the components attributable to NaH or NaI (blue), and diminished amounts of the new component arising from interaction between NaH and NaI (green). (c) I 3d XPS data for the NaH-NaI composite after reduction reaction (black) with the fit (red) and the components attributable to NaI (blue), and diminished amounts of the new component arising from interaction between NaH and NaI (green). (d) C 1s XPS data for the NaH-NaI composite after reduction reaction with the peak at 284.6 eV from the carbon tape substrate being used for calibration of the sample.

Figure 3.3. (a) Na 1s XPS data for the NaH-LiI composite (black) with the fit (red) and the components attributable to NaH or NaI (blue), and the new component arising from interaction between NaH and NaI (green). (b) I 3d XPS data for the NaH-LiI composite (black) with the fit (red) and the components attributable to NaI (blue), and the new component arising from interaction between NaH and NaI (green).

Figure 3.4. (a) Na 1s XPS data for the NaH-NaI composite (black) with the fit (red) and the components attributable to NaH or NaI (blue), and the new component arising from interaction between NaH and NaI (green). (b) I 3d XPS data for the NaH-NaI composite (black) with the fit (red) and the components attributable to NaI (blue), and the new component arising from interaction between NaH and NaI (green). (c) O 1s XPS data for the NaH-NaI composite arising from the acrylate adhesive found in the carbon tape. (d) C 1s XPS data for the NaH-NaI composite with the peak at 284.6 eV from the carbon tape substrate being used for calibration of the sample.

More intriguingly, the I 3d_{5/2} and 3d_{3/2} bands of the NaH-LiI XPS spectrum also appear to consist of two components, one of which is the expected peak for NaI at 618.6 and 629.9 eV (42%), while the other component at 620.3 and 631.6 eV (58%) suggests some unique, higher energy photoemission distinct from a typical monoanionic iodide (Figure 3.3b).^{152,153} The NaH-NaI sample exhibits behavior similar to that of NaH-LiI, with NaI as

the minor component (31%) at 618.6 and 630.0 eV, and a new major component at 620.7 and 632.2 eV (green line, Figure 3.4b) is attributable to the unique NaH-NaI composite.¹⁵³ No significant amounts of Li were detected by XPS measurements. Due to the presence of O 1s signals arising from the acrylate adhesive in the carbon tape, we could not obtain conclusive information about the absence of amorphous forms of NaOH or LiOH.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was undertaken on the composites, but no distinctive band was observed in the mid-IR region, as expected for NaH.¹⁵⁴ However, after the NaH-NaI sample had been employed for a reduction reaction, the ATR-FTIR spectrum revealed the presence of CN⁻ (2086 cm⁻¹) in the bulk material as anticipated.¹⁰³

A set of solid-state ⁷Li, ²³Na, and ¹²⁷I NMR measurements was performed to understand the structures of the NaH-NaI and NaH-LiI composites. We have also measured the NMR spectra of NaH, NaI, and LiI as references. The peak positions in the NMR spectra are very sensitive to the local environment of each nucleus. Thus, if two samples show NMR spectra with the peaks at the same positions, we can safely conclude that the local structures around the observed nuclei are very similar to each other. As shown in Figure 3.5, the ¹²⁷I NMR spectra of the NaI, NaH-NaI, and NaH-LiI samples gave sharp peaks at 177 ppm, which differ significantly from that of LiI (358 ppm). This result clearly shows the remarkable absence of the LiI structure in the NaH-LiI composite. The data also strongly indicates that the local environments of ¹²⁷I are almost the same in the detectable *bulk* environments of the NaI, NaH-NaI, and NaH-LiI samples, suggesting the retention and formation of the cubic NaI structure in both the NaH-NaI and NaH-LiI composites, respectively. The sharp lineshapes of ¹²⁷I NMR spectra indicate the absence of quadrupolar coupling, suggesting that the cubic symmetry in the crystals remains. This agrees with the PXRD observations as well. The ¹²⁷I NMR lineshape also does not change in the absence

and presence of ^1H decoupling (Figure 3.6). These data show that the ^{127}I nuclei are located at greater than several Å away from ^1H in the NaH-LiI and NaH-NaI samples.

Figure 3.5. ^{127}I NMR spectra of (a) LiI; (b) NaI; (c) NaH-LiI composite; (d) NaH-NaI composite. The spinning sidebands signals are marked with asterisks.

Figure 3.6. ^{127}I NMR spectra of (a) NaH-LiI composite; (b) NaH-NaI composite observed with (black) and without (red) ^1H decoupling.

Figure 3.7 illustrates the ^7Li NMR spectra of LiI, LiH, and NaH-LiI composite. The ^1H decoupled ^7Li NMR spectrum of NaH-LiI composite is also shown. All the lineshapes are rather sharp, but due to the small quadrupolar moments in ^7Li , it is inconclusive to be more definitive about the local symmetry in ^7Li based on the lineshapes. Although all the spectra were very similar, closer inspection shows a small difference in the chemical shifts. While LiH (Figure 3.7b) and the NaH-LiI (Figure 3.7c) composition give identical peak positions, the LiI sample (Figure 3.7a) gives a slight shift toward the high-frequency side. This suggests that the ^7Li environment of the NaH-LiI composite is closer to the structure of LiH, rather than that of LiI. The absence of LiI in the NaH-LiI sample agrees with ^{127}I NMR and PXRD observations. The ^1H decoupling improves the resolution in the NaH-LiI spectrum (Figure 3.7c). This clearly demonstrates the presence of proximity between ^1H and ^7Li , consistent with the LiH structure. The $^1\text{H}/^7\text{Li}$ heteronuclear correlation (HETCOR) spectrum (Figure 3.8) of NaH-LiI composite clearly shows the interactions between ^1H and

^7Li . These results also support the presence of LiH and the absence of LiI in the NaH-LiI composite.

Figure 3.7. ^7Li NMR spectra of (a) LiI; (b) LiH; (c) NaH-LiI composite. The comparison with (red) and without (black) ^1H decoupling is also shown. The vertical line is a guide for eye. dec. = decoupled.

Figure 3.8. $^1\text{H}/^7\text{Li}$ HETCOR spectrum of NaH-LiI composite. The ^1H and ^7Li 1D slices at $(^1\text{H}, ^7\text{Li}) = (3 \text{ ppm}, 4 \text{ ppm})$ are also shown. The spinning sidebands signals are marked with asterisks.

In addition, ^{23}Na NMR experiments were conducted for NaI, NaH, and both the NaH-LiI and NaH-NaI composites (Figure 3.9). The NaI and NaH samples give discrete peaks at -2 ppm and 19 ppm, respectively, enabling us to distinguish these two structures from the ^{23}Na peak positions. The observed sharp lineshapes agree with the cubic symmetry in the detectable parts of these samples.

Figure 3.9. ^{23}Na NMR spectra of (a) NaI; (b) NaH; (c) NaH-LiI composite; (d) NaH-NaI composite.

The ^1H decoupled experiments were also performed for NaH, and both the NaH-LiI and NaH-NaI composites (Figure 3.10). The resolution/sensitivity improvement by ^1H decoupling in NaH (Figure 3.10a) is consistent with the proximity between ^{23}Na and ^1H , which is a natural consequence of the crystal structure. We can assign the peak at 19 ppm (-2 ppm) as the NaH (NaI) structure from the ^1H decoupled ^{23}Na spectra together with the peak position without any ambiguity.

These results strongly suggest the coexistence of NaH and NaI in both the NaH-NaI and the NaH-LiI samples as confirmed by the PXRD experiments described above. However, we note that when the cubic symmetry of NaH is disrupted by NaI in a composite, the quadrupolar interactions of the ^{23}Na nuclei will be reintroduced because of the asymmetric environment around ^{23}Na . Consequently, the ^{23}Na NMR signals could have very broad lineshapes that may not be detectable.

Figure 3.10. Comparison of ^{23}Na NMR spectra of (a) NaH; (b) NaH-LiI composite; (c) NaH-NaI composite with (red) and without (black) ^1H decoupling.

We also measured the nutation curve of ^{23}Na of the NaH-NaI sample to see the effect of quadrupolar couplings (Figure 3.11). Although some distortion from a sine curve is observed due to the short repetition delay, both peaks behave similarly to the solution ^{23}Na samples. These experiments also confirm the cubic structure in the NaH-NaI sample through the absence of quadrupolar couplings.

Figure 3.11. The ^{23}Na nutation curve of the NaH-NaI composite.

Overall, the NMR data collectively indicate 1) the coexistence of NaH and NaI in both the NaH-NaI and NaH-LiI composites, 2) the absence of the LiI structure in the NaH-LiI composite, and 3) the possible formation of LiH in the NaH-LiI composite through solvothermal salt metathesis.

3.3 Reaction scope of NaH-NaI composite

Based on the work done in thesis, the applications of NaH-NaI and NaH-LiI composites in the hydrodehalogenation of a wide range of bromo- and iodoarenes under mild reaction conditions have been examined. The detailed mechanistic studies suggested that the hydrodehalogenation proceeds via neither a radical nor a metal-halogen exchange pathway, but through a rather unusual concerted nucleophilic aromatic substitution mechanism.¹⁵⁵ Meanwhile, it was found that the reduction of the alpha-arylacetamide

delivers 3-isopropyl-2-naphthaldehyde in 64% yield, which was reported as an unprecedented example of nucleophilic amination of methoxyarenes by a tethered amine moiety in the presence of NaH-LiI composite. It was found that the resulting sodium amides undergo facile intramolecular substitution of a rather unusual leaving group, a methoxy group on the arenes, to afford benzannulated nitrogen heterocycles with up to ten-membered rings.^{156,157}

3.4 Conclusions

In summary, we have discovered a remarkably simple protocol to prepare a new inorganic composite of NaH-NaI having intriguing nucleophilic hydride donor reactivity. A suite of characterization tools including structural analyses by PXRD, solid-state NMR spectroscopy, XPS allude to the recrystallization of NaI in the presence of NaH in THF. This procedure produces smaller, activated units of NaH, which are dispersed on the cubic NaI crystal phase. Synergistic cooperation between NaH and NaI at the surface of the composite is proposed to be critical for the observed hydride donor chemical reactivity to NaH. The NaH-NaI composite is capable of unprecedented nucleophilic hydride transfer to a broad range of unsaturated substrates, such as nitriles, imines, amides, esters, and carbonyl compounds. It is still in progress to explore further application of the present protocol to develop other kinds of nucleophilic hydride reduction with the NaH-NaI composite, as well as preparations of other new types of inorganic composites from readily available simple materials which are not included in this thesis.

3.5 Experimental section

Sample preparation of NaH-NaI and NaH-LiI composites

To a mixture of NaH and NaI or LiI in a flamed-dried 100 mL sealed tube was added 25 mL of THF in a glovebox. The reaction mixture was stirred at an external temperature of 85 °C. After cooling to room temperature, the THF was removed *in vacuo*. The vacuum-dried powder was rinsed with anhydrous pentane (3.0 mL $\times$ 8) in a glovebox to remove the mineral oil. This sample was used for the powder XRD, XPS, and solid-state NMR experiments. Due to the moisture sensitivity of NaH, it was always handled under N₂ in a glovebox or with Schlenk techniques under N₂ or Ar. Likewise, the sample preparation for NaH and their corresponding composites have been performed in a glovebox under N₂.

Powder X-ray diffraction: The XRD experiments were conducted using Bruker D8 Advance X-ray diffractometers, each equipped with a copper ($K_{\alpha 1}(1.54060)/K_{\alpha 2}(1.54439)$ = 2) target X-ray tube set to 40 kV and 40 mA.

X-ray photoelectron spectroscopy: X-ray photoelectron spectroscopy was measured by using a Phoibos 100 spectrometer (Mg X-ray radiation source (SPECS, Germany)).

Solid-state NMR spectroscopy: All the solid-state NMR spectra were measured by a JNM-ECX400 NMR spectrometer (JEOL Ltd., Tokyo, Japan) equipped with a 4.0 mm HXMAS double resonance probe. The 90° pulse-width in the ¹H, ²³Na, ¹²⁷I, and ⁷Li experiments are 2.7 μ s, 3.7 μ s, 4.0 μ s, and 5.25 μ s, respectively, which are measured with solution samples. The samples were packed into the rotor with great care to avoid air- and moisture-contamination (the samples were packed into the rotor under a N₂ atmosphere just before the NMR measurements).

FTIR spectroscopy: FTIR spectra were recorded on a Bruker ALPHA FTIR spectrometer in a glovebox. The Platinum ATR module was used to collect data on powder samples.

Experimental Details for PXRD

Sample preparation of NaH-NaI composite (before decyanation reaction)

To a mixture of NaH (60% dispersion in mineral oil; 0.60 g, 15 mmol) and NaI (1.5 g, 10 mmol) in a flamed-dried 100 mL sealed tube was added 25 mL of THF in a glovebox. The reaction mixture was stirred for 2 h at an external temperature of 85 °C. After cooling to room temperature, the THF was removed *in vacuo*. The vacuum-dried powder was rinsed with anhydrous pentane (3.0 mL $\times$ 8) in a glovebox to remove the mineral oil. This sample was used for the powder XRD, XPS, and solid-state NMR experiments.

Sample preparation of NaH-LiI composite (before decyanation reaction)

The procedure is similar to the one for NaH and NaI. However, the quantities used were different. In the case of NaH and LiI, NaH (60% dispersion in mineral oil; 0.40 g, 10 mmol) and LiI (0.67 g, 5.0 mmol) were used and the reaction mixture was stirred for 30 m instead.

Sample preparation of NaH-NaI composite (after decyanation reaction)

To a mixture of NaH (60% dispersion in mineral oil; 0.30 g, 7.5 mmol), NaI (0.75 g, 5.0 mmol) in a flamed-dried 100 mL sealed tube was added a solution of 2,2-diphenylpropanenitrile (0.518 g, 2.50 mmol) in 12.5 mL of THF. The reaction mixture was stirred for 24 h at 85 °C. After the suspension was allowed to stand undisturbed at around 60 °C, the particles in the suspension deposited. Before further cooling to room temperature, most of the supernatant was removed via a syringe and the remaining solvent was removed *in vacuo*. The vacuum-dried mixture was taken into a glovebox and washed with anhydrous pentane (3.0 mL $\times$ 8) to remove the mineral oil. This sample was used for the PXRD, XPS, and solid-state NMR experiments.

PXRD experiments

In a glovebox, the vacuum-dried sample was loaded and sealed in an airtight specimen holder. The PXRD experiments were conducted using a Bruker D8 Advance X-ray diffractometer with a copper ($K_{\alpha 1}(1.54060)/K_{\alpha 2}(1.54439) = 2$) target X-ray tube set to 40 kV and 40 mA.

X-ray photoelectron spectroscopy (XPS) experiments

The XPS samples were prepared by coating a uniform layer of the materials on SPI double-sided adhesive carbon tape in a glovebox. The carbon tape contains acrylate adhesives, so both C 1s and O 1s signals are present in the carbon tape itself. The XPS data were processed using the CasaXPS software. The spectra were calibrated internally based on the C 1s position at 284.6 eV. This is because variations of several eV in the reported binding energies have been observed depending on the instrument and the sample preparation procedure.

The experiments on the pristine NaH, NaI, and LiI samples with the same internal calibration were conducted to ensure consistency and reproducibility. These data are crucial to evaluate the relative peak position of these elements in the composite samples.

Figure 3.12. (a) Na XPS data for NaH with the Na 1s signal at 1070.0 eV. (b) O 1s XPS data for NaH arising from the acrylate adhesive found in the carbon tape. (c) C 1s XPS data for NaH with the peak at 284.6 eV from the carbon tape substrate being used for calibration of the sample.

Figure 3.13. (a) Na XPS data for NaI with the Na 1s signal at 1070.2 eV. (b) I 3d XPS data for NaI with the $I\ 3d_{5/2}$ signal at 618.8 eV and the $I\ 3d_{3/2}$ signal at 630.2 eV. (c) O 1s XPS data for NaI arising from the acrylate adhesive found in the carbon tape. (d) C 1s XPS data for NaI with the peak at 284.6 eV from the carbon tape substrate being used for calibration of the sample.

Figure 3.14. (a) I 3d XPS data for LiI with the I 3d_{5/2} signal at 618.0 eV and the I 3d_{3/2} signal at 629.5 eV. (b) O 1s XPS data for NaI arising from the water of crystallization in LiI and the acrylate adhesive found in the carbon tape. (c) C 1s XPS data for LiI with the peak at 284.6 eV from the carbon tape substrate being used for calibration of the sample.

In order to analyze the composition of the composite in a quantitative manner, Rietveld refinement was performed, and the fitting parameters are shown below.

Table 3.1. Rietveld refinement results on the powder X-ray diffraction data for the NaH and NaI composite samples.

	Atom	Site	x	y	z	Occupancy	B _{eq.}
NaH + LiI							
R _{wp} : 7.02							
GOF: 1.15							
NaH	Na	4a	0	0	0	1	1
Fm-3m (No. 225)							
a: 4.8811(4)							
R _B : 4.09	H	4b	0.5	0.5	0.5	1	1
wt: 26.5%							
NaI	Na	4a	0	0	0	1	1
Fm-3m (No. 225)							
a: 6.4730(3)							
R _B : 3.84	I	4b	0.5	0.5	0.5	1	1
wt: 73.5%							
NaH + NaI							
R _{wp} : 15.6							
GOF: 1.34							
NaH	Na	4a	0	0	0	1	1
Fm-3m (No. 225)							
a: 4.8815(4)							
R _B : 13.7	H	4	0.5	0.5	0.5	1	1
wt: 36.9%							

NaI	Na	4a	0	0	0	1	1
Fm-3m (No. 225)							
a: 6.4733(3)							
R _B : 6.42	I	4	0.5	0.5	0.5	1	1
wt: 63.1%		b					

NaH + NaI after reaction

R_{wp}: 11.4

GOF: 1.14

NaH	Na	4a	0	0	0	1	1
Fm-3m (No. 225)							
a: 4.8786(7)							
R _B : 6.93	H	4	0.5	0.5	0.5	1	1
wt: 18.8%		b					

NaI	Na	4a	0	0	0	1	1
Fm-3m (No. 225)							
a: 6.4698(4)							
R _B : 2.22	I	4	0.5	0.5	0.5	1	1
wt: 81.2%		b					

To probe the surface content of the composite materials, XPS was conducted on the composites (Figures 3.3 and 3.4) as well as pristine samples of NaH, NaI, and LiI (Figures 3.12-3.14 respectively, and Table 3.2). All the XPS data have been calibrated internally to the C 1s signal from the carbon tape used and were fitted to reveal more accurate results.

Table 3.2. XPS fitting data for the mixed NaH and NaI composites and pristine samples of their constituents. The new components in the composite are highlighted in bold.

Sample	Species	Binding Energy (eV)	FWHM (eV)	% Composition
NaI	Na 1s	1070.2	2.0	100
	I 3d _{5/2}	618.7	1.9	55.9
	I 3d _{3/2}	630.1	2.1	44.1
NaH	Na 1s	1070.0	2.0	100
LiI	I 3d _{5/2}	618.1	1.8	58.3
	I 3d _{3/2}	629.5	1.9	41.7
NaH + NaI	Na 1s	1069.8	2.6	56.4
		1072.4	2.3	43.6
	I 3d _{5/2}	618.6	2.4	16.3
		620.7	2.2	39.9
	I 3d _{3/2}	630.0	2.4	14.2
		632.2	2.2	29.6
NaH + NaI after reaction	Na 1s	1069.6	1.8	94.4
		1071.7	1.8	5.6
	I 3d _{5/2}	618.6	1.7	54.3
		621.1	1.7	4.4
	I 3d _{3/2}	630.0	1.7	38.8
		632.4	1.7	2.5
NaH + LiI	Na 1s	1069.5	2.3	74.5
		1072.0	2.0	25.5
	I 3d _{5/2}	618.6	2.2	26.1
		620.3	2.2	31.3
	I 3d _{3/2}	629.9	2.2	18.7
		631.6	2.2	23.8

Solid-state NMR measurements

The solid-state ^7Li , ^{23}Na , and ^{127}I NMR measurements on the NaH-NaI and NaH-LiI composites were conducted, with NaH, NaI, and LiI as references. The peak positions will be very sensitive to local environments. Moreover, the line shapes of the NMR peaks provide information about the symmetry of the local environments. Since the ^7Li , ^{23}Na , and ^{127}I are all half-integer quadrupolar nuclei, the NMR peaks will suffer from second-order quadrupolar broadening. However, the cubic symmetry can remove the quadrupolar interaction due to the zero electric-field gradient at the nuclei, resulting in sharp peaks even for these quadrupolar nuclei. Thus, sharp peaks of half-integer quadrupolar nuclei indicate the local cubic symmetry. This can be further confirmed by nutation measurements. The oscillation of the nutation curve should be the same as that of NMR experiments in solution, if the quadrupolar interactions are absent or negligible, otherwise the oscillation becomes quicker than the solution NMR. The NMR spectra can also produce insights about the connectivity between two nuclei. When the NMR experiments are conducted with and without ^1H decoupling, it can be monitored the proximity between the ^1H and the other nuclei. If the resolution (and thus sensitivity) of the NMR spectra is improved by ^1H decoupling, the nuclei should have close interactions with ^1H . This can be further supported by two-dimensional (2D) $^1\text{H}/\text{X}$ heteronuclear correlation (HETCOR) measurements, which directly correlate the ^1H and the NMR peaks of the other X nucleus. The X NMR peak will disappear if X does not have any interactions with ^1H .

The ^{127}I NMR spectra of the LiI, NaI, NaH-NaI, and NaH-LiI composites (Figure 3.3) were also measured. Since the NaH-NaI and NaH-LiI composites include hydrogen, we also measured the ^{127}I NMR spectra with ^1H decoupling for these two samples to gauge the proximity between ^1H and ^{127}I . The LiI and NaI show very sharp peaks at 358 ppm and 177 ppm, respectively. The sharp peaks in these samples, which allude to the absence of

quadrupolar interactions, are consistent with the local cubic symmetry of the nuclei. As described in the main text, the local environments of ^{127}I are almost the same for NaI, NaH-NaI, and NaH-LiI, suggesting that the same cubic structure exists in the detectable bulk sample of both the NaH-NaI and NaH-LiI composites.

Summary and outlook

In this thesis, three main projects were designed and thoroughly investigated. Firstly, to achieve the development of artificial photosynthesis, potential earth-abundant photosensitizers were proposed and assessed. Metal halide perovskites have been evaluated as potential candidates especially for solar cells, regardless of the fact that most of the derivatives suffer from poor stability towards protic media. The practical applications of these promising materials are drastically limited particularly in a photosynthetic system. Therefore, in the first chapter, targeting specifically the improvement of stability of perovskite materials, a few novel 2D perovskites were designed, synthesized and fully characterized. More importantly, some of these perovskites were successfully employed as photocatalysts in photoredox catalysis for valuable organic reactions including dehydrogenation and decarboxylation. In the second chapter, the scalability of perovskite materials was discussed, and a feasible solvent-free method was developed featuring mechanochemistry to facilitate the synthesis of perovskites up to kg scale. This method reveals the potential of metal halide perovskites to be commercialized in a mass market. Moreover, it also demonstrates an essential approach to utilize energy in a much more efficient way for the purposes of materials synthesis.. In the last chapter, due to the very unique hydride transfer behavior of NaH-NaI composite in decyanation and dehalogenation reactions, thorough characterization using various advanced techniques was carried out. The special feature was found to originate from nanocrystalline NaH with their crystal lattice interrupted by iodine atoms spreading over. This work highlighted the value of this system in the context of green chemistry due to the avoidance of using heavy metal complexes or harsh reaction conditions for similar reactions.

Beyond this thesis, more mechanistic studies can be conducted on the photocatalysis by 2D perovskites, and these materials can be applied for a broader range of reactions. It will be desirable if the intermediate radicals generated can be further utilized for C-C coupling reactions that yield more valuable products. Regardless of the improved stability, the intrinsic limit of these 2D perovskite materials persists as a challenge for the broader application of these materials. The sensitivity of these materials to basic conditions, under which the ammonium cations can be deprotonated leading to the collapse of the 2D structure, narrows the substrate scope to mainly neutral compounds. However, these materials demonstrate higher potential to be employed in a mixed cation system for the photovoltaic devices.

Mixed cation perovskites have been found to be much more stable than the pure MA perovskites with comparable device performances. It was theorized that FA, Cs⁺ and Rb⁺ cations are able to stabilize the perovskite structure thermodynamically by shifting the equilibrium towards a new state.^{158,159} Based on the hydrophobic feature that has been successfully developed in this thesis, coupled with feasible synthesis using low boiling point solvent, it is proposed to be a promising approach for the fabrication of mixed-cation metal halide perovskites.⁷¹ It is also believed that high quality thin films and devices can be produced via this simple preparation method. We expect that the composition of these Ruddlesden-Popper (RP) perovskites can be finely engineered.^{160,161} The desired products are hypothesized to behave as effective light absorbers which are capable to provide excellent protect from ambient conditions for photoelectronic devices. It is also anticipated to achieve a better efficiency in harvesting photons using these panchromatic photosensitizers in photocatalytic systems. However, these RP perovskites are argued to suffer from poor charge separation due to the 2D layered structures, which causes inferior performance in a solar cell. Regardless of this debate, recent studies provide promising

demonstrations of RP type perovskite solar cells achieving high efficiency over 15%.^{162,163} Inspired by these research, it is speculated that HDA based perovskites can be perfect candidates as the building blocks for RP perovskites. With the hydrophobicity of HDA perovskites, the resulting solar cells are expected to be highly stable at ambient conditions. Detailed engineering and optimization of these devices have to be conducted in order to achieve the high performance. Hence, the author looks forward to a thorough study of HDA based perovskites as an essential building block that contributes in the industry of perovskite solar cells.

While the enthusiastic research on lead-based perovskites continues to blossom, the toxicity of these perovskites has emerged as one of the top issues relating to the real-world applications. It was well studied that even minimal exposure to lead may cause chronic impairment to our neuron system due to the high coordinating ability of lead to certain proteins by replacing calcium cation within the critical neuro signaling process.¹⁶⁴⁻¹⁶⁶ The water solubility of lead halide compounds makes it even easier to penetrate and spread into the environment which causes a more hazardous impact.¹⁶⁷ It is highly chanted to introduce encapsulation for lead-based devices when the time comes for them to be fully commercialized and mass produced.¹⁶⁸ Nevertheless, we certainly have to take the cost of these safety protocols into consideration.

Consequently, it gets rather urgent to develop alternative perovskites based on other earth-abundant metals that are less toxic. Sn(II) based perovskites have been studied but the intrinsic tendency to oxidation has severely prevented their further applications.^{169,170} Bismuth has been proposed to be an ideal candidate for the choice of metal due to its nearly non-toxic nature to living species.¹⁷¹ The initial application of $[(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{Cl}_9]_n$ in solar cell has been developed and the results indicate promising performance while the stability

is determined to be remarkable.¹⁷² Another promising approach is a 1D bismuth-based perovskite using aliphatic diamines as intercalating organic layers.¹⁷³ Zhang W. et al. have found this lead-free 1D hybrid perovskite to be a potential light absorber with a narrow band gap of 2.02 eV. The high stability under ambient conditions of this materials also highlights its promising role as a candidate of photosensitizer, which could be a potential direction to extend the research scope based on this thesis.

Moreover, with the expectation of a high demand of perovskite materials in the future, the mechanochemical approach established in Chapter II can be incorporated as a competitive industry solution due to the scalability and high energy efficiency. While only limited candidates of perovskites were included herein to demonstrate the capability of this method, it is believed that this method can be applied to a vast majority of inorganic and hybrid perovskite materials. It is also worth noticing that the ease of this method is matchless when it comes to the fabrication of sophisticated materials with complicated compositions. The application of these mechano-synthesized perovskites is currently focused on photodetectors as a proof of concept, although the performance of these devices is still far inferior to the finely optimized thin-film counterparts. It certainly requires detailed optimization of the device fabrication process, before a much broader application of this approach can be realized.

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List of publications

1. Yang L., Hong Z., Wu J., Zhu L.W., Facile production of a large-area flexible TiO₂/carbon cloth for dye removal, *RSC Adv.* **2014**, 4, 25556-25561
2. Hong, Z. Ong, D. Y. Muduli, S. K.; Too, P. C. Chan, G. H. Tnay, Y. L. Chiba, S. Nishiyama, Y. Hirao, H. Soo, H. S. Understanding the origins of nucleophilic hydride reactivity of sodium hydride-iodide composite, *Chem. Eur. J.* **2016**, 22, 7108-7114
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