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POLARIZATION-SENSITIVE PHOTODETECTORS BASED ON HYBRID ORGANIC-INORGANIC PEROVSKITES

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2025

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Polarization-Sensitive Photodetectors Based on Hybrid Organic-Inorganic Perovskites

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

August 2024

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Abstract

Polarization-sensitive photodetectors are garnering significant attention due to their applications in medical science, bio-signal detection, astronomy, display technology, and quantum computing. They can be divided into linearly-polarized-light (LPL) photodetector and circularly-polarized-light (CPL) photodetector. Organic-inorganic hybrid perovskites (HOIPs), a group of materials characterized by their high absorption coefficients and long carrier diffusion lengths, are promising candidates for both LPL photodetectors and CPL photodetectors. LPL photodetectors based on HOIPs can be realized by using HOIPs with intrinsically anisotropic crystal structures or by combining HOIPs with other materials that have anisotropic crystal structures into heterojunctions, or by forming perovskites with anisotropic morphology, such as nanowires (NWs). However, synthesizing large-scale and high-quality HOIP crystals with an anisotropy crystal structure is challenging and time-consuming. Fabricating HOIP NWs also requires complex techniques. Additionally, the optoelectronic performance of LPL photodetectors requires further enhancement. CPL HOIP photodetectors are typically built on chiral HOIPs, which exhibit CPL-sensitive optical absorption and efficient charge carrier transport. Research on chiral HOIPs for photodetectors has focused on one-dimensional (1D) and two-dimensional (2D) chiral HOIPs, which feature relatively wide bandgaps. However, materials with tunable bandgaps and broad response regions are preferred for photodetectors. While significant efforts have been made to investigate chiral HOIPs with tunable bandgaps, IV

materials that offer a broad response region and exceptional photoelectric properties still need further exploration.

In this thesis, first, we fabricated an LPL photodetector based on nanoimprinted quasi-2D HOIP thin films with vertical gradient phase distribution. The nanoimprinting method is utilized to create nanoscale linear patterns on the surface of the film. It enables polarized light detection and enhances absorption. According to the results of transient absorption analysis, a vertical gradient phase distribution along the longitudinal direction of quasi-2D HOIP $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (PEA^+) =C₆H₅CH₂CH₂NH₃⁺, MA⁺ = CH₃NH₃⁺, n = 3) is confirmed, which facilitates efficient carrier transfer and separation, leading to improved device performance. These detectors demonstrate outstanding photo-response with a large responsivity of ~90 A/W and a high detectivity reaching the order of 10^{12} Jones. The photoluminescence of the quasi-2D HOIP film exhibits an anisotropy ratio of 2.05, and the LPL photodetector reaches a polarization sensitivity of 1.68. These findings offer insight into the feasibility of developing HOIP materials for photodetectors, which have potential applications in imaging, sensing, and communication technologies.

Second, we prepared chiral HOIP films with a wide distribution of multiple quasi-2D phases to achieve broadband CPL photodetectors. The chiral ligands S/R-MBA (S/R-MBA=S/R-methylbenzylammonium, C₆H₅CH(CH₃)NH₂) introduced chirality into the

HOIP films. We encountered challenges obtaining quasi-2D phases within (S-MBA)₂MA_{n-1}Pb_nI_{3n+1} films, as the n = 1 phase and the three-dimensional (3D) phase consistently predominated. However, when both PEA and S/R-MBA were introduced in the film, the (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films exhibited multiple quasi-2D phases and demonstrated CD signals in a broad range. We investigated the optoelectronic performance of photodetectors based on (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films with varying ligand ratios and successfully fabricated a CPL photodetector using the (R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ film. This photodetector shows a broadband photoresponse and achieves a high responsivity of 1.07 A/W under 0.742 mW/cm² illumination at 447 nm. Additionally, it exhibits CPL sensitivity over a wide wavelength range. The anisotropy factor of photocurrents (g_{1ph}) under 447 nm, 532 nm, and 633 nm CPL illumination was measured to be 0.11, 0.19, and 0.10, respectively.

Third, we synthesized chiral quasi-2D HOIP crystals, specifically (S/R-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI_{3n+1} with n = 1, 2, and 3. We characterized and compared these crystals' chiroptical and photoelectric properties with varying quantum well thicknesses. The crystals with n = 1, 2, and 3 were fabricated into CPL photodetectors, achieving anisotropic factors of 0.18, 0.28, and 0.16 under 520 nm, 532 nm, and 633 nm illumination, respectively. This work provides insights into the components of the (S/R-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI_{3n+1} films discussed in Chapter 4 and introduces a new design strategy for chiral multilayered HOIPs in the field of CPL detection.

List of Publications

(1) Liu, D., Wei, Q., Zhuang, L., Liu, M., Zeng, L., Ren, H., Li, M., Lau, S. P. (2024).

Nanoimprinted Quasi-2D Perovskites toward High-Performance Polarization-Sensitive Photodetectors. *Advanced Optical Materials*, 12(11), 2302411

Acknowledgements

First, I give sincere gratitude to my supervisor, Professor S.P. LAU. He provided crucial help in my PHD period. First, he accepted me as a group member when I needed guidance and support the most. Second, he gave me long-sighted advice on research directions. He allowed me to choose my preferred area and gave me more specific advice. With the research, I understood that the direction he recommended is important and closely integrated with applications, which is what I want. Besides, it turns out that the direction he pointed out was getting more research attention in the following years. Third, he never put heavy pressure on me or gave me any work unrelated to my research, although this is not ubiquitous nowadays. As he said in our first meeting, the essential requirement for a doctoral student is not complicated: the ability to carry out research work independently. He has always cultivated me based on this principle, neither slacking off nor going too far. Fourth, in the group he leads, members work together efficiently with an open and friendly atmosphere. Thanks to this, I progressed in my research and gained friendships here. This leadership style impressed me, and I believe it will positively impact my future career.

Second, I would like to thank Dr. Wei Qi, a postdoctoral researcher in our department. He provided constructive suggestions for my research, and we collaborated on a project. When I started my first work, I was a green hand in many optical experiments and related theories. Although Dr. Wei Qi was not a member of our group, he pointed out VIII many problems in my research out of concern for juniors. Even though my questions were always straightforward, he remained patient and provided detailed explanations. In my first work, he conducted a transient absorption experiment and carrier diffusion length measurement, which is necessary to support our points. I remember he worked on these experiments until midnight those nights, even though he was already fully scheduled. Due to his deep experience in his research field, he is familiar with multiple subdivisions. He often suggested me pay attention to some researchers and recommended me make some attempts. These suggestions helped me proceed very quickly.

Third, I would like to thank Dr. Zhuang Lyuchao, a postdoctoral researcher in our group. I had a great experience during my days in college, and he was integral to that. First, we have somewhat related topics and often discuss them together. He entered this research field two years before me and has a deeper understanding of many issues than me. He was willing to hand over his experience and knowledge to me without reservation and was very concerned about my progress. He always guided me when I needed to perform unfamiliar experiments, even though it was time-consuming. He would introduce me to others who might help if it was beyond his capabilities. Second, he advised me to keep a work-life balance. He often invited me to join activities like jogging, hiking, and city walks. These activities objectively helped me maintain an optimistic attitude toward my work. In addition, he often gave me some advice on my personal life. His maturity and stable mentality impressed me.

Fourth, I thank Miss Chen Hongye, Miss Ren Hui, and Mr. Chen Tianren. They gave kind help and important advice in device fabrication, material preparation, and device measurement. Also, I give gratitude to Dr. Li Mingjie, Dr. Shi Fangyi, Dr. Liu Ming, Mr Xiao Yiping, Miss Chen Ziling, Mr Liu Yuan, Miss Lao Xinyue, Miss Li Lu, Mr. Han Meizhao, Dr. Loi Hok Leung, Dr. Li Hao, Dr. Wang Chenhao, Mr. Liu Qi, Dr. Jin Yuanyuan, Dr. Li Chuanzhao, Dr. Lin Jun, all Prof. LAU group members, and many friends provides advice to my research. Finally, my love for my dear family is the most important. Their support is necessary for my research life.

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Chapter 1 Introduction

1.1 Background

A polarization-sensitive photodetector is a device capable of measuring the polarization state of light. As a vector property, the polarization of light carries vectorial information, which holds unique significance in various fields. Here are a few typical scenarios where polarization analysis proves valuable. In quantum physics, it is important to characterize quantum channels to enhance the understanding of quantum communication. Polarized light can provide detailed information about the quantum channel properties and enables precise manipulation of the quantum states, allowing for better characterization of quantum channel behaviors.¹ In medical physics, polarized light is an efficient diagnostic tool.² Polarized light-scattering spectroscopy helps researchers differentiate between healthy and diseased tissues and provides insights into the structural organization of epithelial tissues.³ Besides, polarized light in endoscopic scanning spectroscopy can enhance the contrast of the tissue images, ensuring that dysplastic areas are targeted effectively.⁴ In pharmaceutical science, polarized light can be used to analyze the optical activity of chiral drugs, helping to determine their enantiomeric purity and conformational properties. Furthermore, polarized light can provide insights into chiral drugs' molecular orientation and conformation, aiding in the qualitative analysis of their structures.⁵

Previously, polarization-sensitive detectors required the optical component to distinguish polarization. By adjusting the angle of the polarizer and/or the quarter-wave plate, the light intensity sensed by the detector changes depending on the polarization state of the light. Modern photodetector designs focus on eliminating optical components to reduce the size and structural complexity of the device. For this purpose, there are two main approaches:⁶ employing materials with anisotropic crystal structures as absorber layers and introducing microstructures with polarization-sensitive effects. Organic-inorganic hybrid perovskites (HOIPs) are a group of materials with a basic structure of ABX₃, where A represents organic cations such as methylammonium (MA⁺, CH₃NH₃⁺,) and formamidinium [FA⁺, CH(NH₂)₂⁺], B represents metal cations such as lead (Pb²⁺) and tin (Sn²⁺), X represents halide anions such as iodide (I⁻), bromide (Br⁻), and chloride (Cl⁻). Due to their outstanding optoelectronic characteristics, such as high absorption coefficient⁷ and long carrier diffusion length,⁸ OIHPs play important roles in fields like solar cells, light-emitting devices, and memory storage, and they are also promising candidates for polarization-sensitive photodetectors. Significant efforts are currently focused on enhancing the performance metric of HOIP polarization-sensitive photodetectors, such as responsivity and anisotropic ratio.

1.2 Light polarization

1.2.1 Classification of polarization

The nature of light is electromagnetic waves. Various properties, including frequency, amplitude, phase, and polarization, can characterize a ray of light. The frequency represents the energy of a photon and determines the color we see. The amplitude represents the density of photons and determines the intensity of light. The phase refers to the position of a point in the light wave's cycle at a given moment in time and describes the wave's oscillation. Polarization, a vector property, describes orientation of the electric field vector in a light wave. Natural light sources like the sun and burning wood generally emit unpolarized light. However, with reflection, refraction, scattering, and absorption of light, light waves oscillate predominantly in a particular direction, leading to polarization. Polarization can be generally classified into four conditions: unpolarized light, partially polarized light, linearly polarized light (LPL), elliptically polarized light, and circularly polarized light (CPL). In linear polarization, the light wave's electric field oscillates in a single plane, as shown in Figure 1.1a. In circular polarization, the electric field rotates clockwise (right-handed) or counterclockwise (left-handed) in a circular motion as the wave propagates, as shown in Figure 1.1b. When unpolarized light passes through a polarizer, only the light waves that align with the polarizer's transmission axis are transmitted, resulting in linear polarized light. If this linearly polarized light passes through a quarter-wave plate at a 45° angle to the





Figure 1.1 a) Linearly polarized light with a wavelength of λ , polarized in the vertical plane, showing the electric-field vectors perpendicular to the direction of propagation through space. b) circularly polarized lights with left and right circular polarizations, respectively. c) The transition from unpolarized light to linear polarized light to circularly polarized light.^{9, 10}

1.2.2 Application of polarization

Obtaining information by sensing the polarization of light is a specialty of some

creatures in nature. Many butterflies have specialized photoreceptors that allow them to detect polarized light, and they use polarized light patterns on their wings to communicate with potential mates.¹¹ Mantis shrimps have circularly polarized body patterns and possess advanced visual capabilities of sensing polarized light to sense their species.¹² There are many applications of light polarization, such as polarized imaging technology, which refers to capturing images using polarized light. When natural light reflects off a surface, the polarization state can be changed in different ways depending on the property of the surface. Polarized imaging can locate objects by detecting the unique polarized angle of reflected light from the object. For example, by analyzing long-wave IR polarization images, the artificial target presents a strong contrast with the environment.¹³



Figure 1.2 a) Photographs of two butterflies. The image of the left wings is unmodified, and the right wings were generated by taking two photographs through a polarizing filter that was rotated by 90° between exposures. b) Photopolarimetry of mantis shrimp Gonodactylaceus falcatus. The color represents angle of polarization. c) Visible picture

of two pickup trucks in the shade (top) and long-wave IR polarization image (bottom). Strong contrast in the polarization image shows advantages for enhanced target detection using imaging polarimetry. ¹¹⁻¹³

1.3 Photodetectors

1.3.1 Mechanism

A Photodetector is a device that converts light signals into electrical signals. The mechanism of photodetectors generally includes photoconductive effects and photovoltaic effects. The photoconductive effect means the electrical conductivity of a semiconductor rises (namely, the resistance declines) when it absorbs light because photons generate charge carriers (electrons and holes) in the semiconductor. The photovoltaic effect refers to the phenomenon that light generates charge carriers in a semiconductor, then electrons and holes separate in a P-N junction and create a potential difference. Photodetectors based on photoconductive and photovoltaic effects are also called photoconductors and photodiodes.¹⁴



Figure 1.3 Device structure diagrams of a) photoconductor, b) photodiode, and the corresponding carrier movements under light.¹⁴

Photoconductor

The semiconductor material is always placed in the channel between a pair of electrodes (source and drain) for a photoconductor. When operating a photoconductor, a bias voltage is always required. No photogenerated carrier exists in the semiconductor in darkness, so the conductor possesses low charge carrier density and high resistance. In contrast, with illumination, light excites electrons and produces photogenerated charge carriers in the semiconductor. With additional charge carriers, the resistance of the semiconductor decays. As a result, the photoconductor gets a higher current with illumination than in darkness. The difference between the currents under illumination and darkness is called photocurrent. Information about the light intensity, wavelength, and other properties can be obtained by analyzing the photocurrent.

It is worth noticing that the photogating effect is an important phenomenon for photoconductors. It refers to the prolonged carrier lifetime induced by defects, impurities, or other designed structures.¹⁵ This phenomenon commonly occurs in photoconductors fabricated with two-dimensional materials or their heterojunctions. Some localized states always exist in those materials, such as surface, interface, and defects. Those localized states can trap photogenerated carriers and prolong the carrier's lifetime. On the one hand, the photogating effect can improve photocurrents in the photoconductor, but on the other hand, it decreases the response speed. Sometimes, the photogating effect can be a determining factor in the performance of a photoconductor.

Photodiode

Unlike photoconductors, photodiodes always adopt a vertical architecture similar to solar cells. When a photon excites the semiconductor and generates electron-hole pairs in a P-N junction or a Schottky barrier, electrons, and holes can be separated by the built-in electric field and move towards opposite directions. Photodiodes require no bias in operation. Photodiodes typically exhibit an asymmetric current-voltage characteristic (rectifying behavior) in the dark. However, under illumination, they can operate in two modes: the photovoltaic mode and the photoconductive mode. In the photovoltaic mode, which occurs at zero bias, the built-in electric field at the junction separates electron-hole pairs, generating photocurrents. Photodiodes in this mode have the lowest dark current, enhancing detectivity. In the photoconductive mode, which 18 occurs under reverse bias, the external electric field aligns with the built-in electric field, improving the separation efficiency of electron-hole pairs. Benefiting from the reduced carrier transit time and the low diode capacitance, photodiodes in this mode present high response speed.

Besides photoconductors and photodiodes, there are also photodetectors based on other mechanisms, such as the photothermoelectric effect, which converts light into an electrical voltage by generating a temperature gradient in a material.¹⁶

1.3.2 Performance parameters of photodetectors and polarized photodetectors

People defined several performance parameters to characterize photodetectors' performance from different perspectives. Those parameters are important when selecting the appropriate photodetector for a specific application. Here are some key performance parameters of photodetectors:

Responsivity (*R*), the parameter measuring the electric output per unit of optical input power, is defined as $R = \frac{(I_{light} - I_{dark})}{PS}$. Here I_{light} is the current under illumination, I_{dark} is the current in the dark, *P* is the light intensity, and *S* is the effective area. The unit of *R* is A/W. Higher responsivity indicates that the photodetector converts light into an

electrical signal more efficiently.

Quantum Efficiency (QE) is the ratio of the number of photogenerated charge carriers to the number of incident photons. To evaluate a photodetector, we always use external quantum efficiency (EQE) defined as $EQE = \frac{N_I}{N_P}$, where N_I is the number of photogenerated charge carriers flowing through the device per unit time, N_P is the number of photons hitting the effective area of the device per unit time. Higher quantum efficiency indicates more effective photon-to-electron conversion in the photodetector.

Response time refers to a photodetector's response time to a change in light intensity. It contains rise time (τ_r , the photocurrent rising from 10% to 90% of the final value) and decay time (τ_d , the photocurrent declining from 90% to 10% of the final value). A shorter response time means a higher speed of photoresponse.

Detectivity (*D**), a normalized measure of a photodetector's sensitivity, is defined as $D^* = \frac{\sqrt{BA_d}}{NEP}$. Here *B* is the bandwidth, A_d is the bandwidth, *NEP* is the noise equivalent power. *D** can also be approximated by $D^* = \frac{R\sqrt{S}}{\sqrt{2eI_d}}$. The unit of *D** is Jones (cm·Hz^{0.5}/W). A higher *D** indicates better performance in weak light detection.

Linear dynamic range (LDR) is a range of light intensity in which the photodetector can linearly convert incident light into an electrical signal. In other words, the 20 photodetector can maintain a linear relationship between light power density and photocurrent in the range between the lowest and highest light intensities. It is always described by LDR (dB) = $20lg \frac{I_{max}}{I_{min}}$, where I_{max} and I_{min} are the upper and lower limits of the photocurrent in a particular range. A wide linear dynamic range ensures detection accuracy in different light intensities.

For polarized photodetectors, the anisotropic factor of photocurrents is another key factor. For linearly polarized photodetector, the anisotropic factor is the ratio between the maximum and minimum photocurrent under illumination with 0° to 180° polarized angle. A higher anisotropic factor means higher sensitivity to the polarized angle of linear polarized light. For circularly polarized photodetector, the anisotropic factor of photocurrents is defined as the absolute value of $g_{Iph} = \frac{2(I_R - I_S)}{I_R + I_S}$, where Is and IR represent the photocurrents under LCP and RCP illumination, respectively.

1.4 Hybrid organic-inorganic perovskites

Perovskites, named for Russian mineralogist Lev Perovski in 1839, first refers to the mineral discovered in the southern Ural Mountains with a chemical formula CaTiO₃.¹⁷ What people call perovskite today usually refers to a series of materials with a crystal structure of corner-linked octahedra and following the chemical formula ABX₃, as shown in Figure 1.4a.¹⁸ Hybrid organic-inorganic perovskites (HOIPs), as a class of

perovskites combining organic and inorganic components within a perovskite crystal structure, have become an attractive topic in the past years. For HOIPs, generally, A is an organic cation, such as methylammonium (MA⁺, CH₃NH₃⁺,) or formamidinium [FA⁺, CH(NH₂)₂⁺]. B is a metal cation, such as lead (Pb²⁺) or tin (Sn²⁺). X is a halide anion, such as iodide (I⁻), bromide (Br⁻), or chloride (Cl⁻). Metal cations (B) and halide anions (X) form octahedral BX₆ inorganic groups and halide anions are located at the apex of octahedrons. Organic cations (A) are distributed outside the octahedrons. Figure 1.4b presents a photograph of typical HOIP MAPbI₃.



Figure 1.4 a) Schematic of the HOIP structure. b) Photograph of a MAPbI₃ bulk single crystal. Natural facets of the crystal were indexed.^{18, 19}

The classic structure above is called the three-dimensional (3D) structure of HOIPs. Based on 3D structure, HOIPs can be controlled to construct lower dimensional structures by inserting organic chains (spacers) into the octahedra layers. Using n to represent the number of layers between spacers, when the octahedra frameworks are separated into monolayer-octahedra structures (n = 1), we call that two-dimensional (2D) structure. When the octahedra frameworks are separated into multilayer-octahedra 22 structures ($1 \le n \le \infty$), we call that quasi-two-dimensional (quasi-2D) structure. 2D and quasi-2D perovskites can be regarded generated from "slicing" 3D perovskites along the crystallographic planes $\le 100 >$, $\le 110 > or \le 111 >$.²⁰ The $\le 100 >$ oriented 2D perovskite exhibits a high tolerance to both inorganic and organic components, resulting in greater compositional diversity.²¹ Based on its structural characteristics, the $\le 100 >$ oriented 2D and quasi-2D HOIPs can be further classified into several categories, such as Ruddlesden-Popper (RP) HOIP and Dion-Jacobson (DJ) HOIP. The structure formulas of RP and DJ perovskites are A'₂A_{n-1}B_nX_{3n+1} (RP),²² A'A_{n-1}B_nX_{3n+1} (DJ),²³, respectively. The difference between the structures of RP HOIPs and DJ HOIPs is that RP perovskites form double layers between the perovskite slabs with large, typically monovalent organic cations. In contrast, DJ perovskites form single layers with divalent organic cations.^{23, 24} Figures 1.5a and 1.5b presents Schematic of crystal structures of DJ perovskites and RP perovskites, respectively.



Figure 1.5 Schematic of crystal structures of a) Dion-Jacobson perovskite and b) Ruddlesden-Popper perovskite. c) RP perovskite structures with $n = 1, 2, 3.^{22, 24}$

The primary focus of our thesis is on RP HOIPs. For RP HOIPs following the formula A'₂A_{n-1}B_nX_{3n+1}, A' represents the monovalent cation spacers such as insulating nbutylammonium (BA) and phenethylammonium (PEA). A represents an organic cation, such as MA⁺ or FA⁺. B is a metal cation, such as Pb²⁺ or Sn²⁺. X is a halide anion like I⁻, Br⁻, or Cl⁻. The subscript n represents the number of BX₆ layers between the insulating organic spacer layers. Figure 1.5c illustrates the RP HOIP crystal structures packing along the long crystallographic axis with n increasing. In RP HOIPs, the unit layers are stacked together by van der Waals forces to ensure structural integrity. The phase-pure 2D perovskite (n = 1) exhibits strong quantum and dielectric confinement, which hinders carrier transport. As the value of n increases, the photovoltaic properties of quasi-2D (n > 1) perovskites are improved.²⁵ Existence of organic insulating layers in RP HOIPs is a double-edged sword for optoelectronic applications. On the one hand, the spacer molecules always contain hydrophobic aliphatic or aromatic groups, inhibiting perovskite crystal lattice degradation. On the other hand, the quantum well (QW) structure caused by the insulating layers increases the exciton binding energy and inhibits the dissociation of photogenerated charge carriers.

1.5 Polarized photodetector based on HOIPs

1.5.1 LPL HOIP photodetector

There are generally two kinds of methods to realize linearly polarized light detection with perovskites: First, using perovskites with anisotropic crystal structures or combining perovskites with other materials with anisotropic crystal structures; second, forming perovskites with anisotropic morphology, especially nanowires (NWs).

Linearly polarized perovskite photodetector based on anisotropic crystal structure

Employing perovskite crystals with high in-plane anisotropy and outstanding photoelectric properties to prepare devices is a reliable method to achieve linearly polarized photodetection. The anisotropy in crystal structures is connected with optical properties because electrons in covalent bonds are affected by electric fields, so the anisotropy of covalent bonds in a material affects the material's absorption of light, promoting optical anisotropy. Fang and coworkers synthesized 2D perovskite FAGPbI4 crystals with large optical anisotropy, as shown in Figure 1.6a.²⁶ The as-synthesized crystals exhibited a photocurrent linear dichroic ratio of 2 and a PL linear dichroic ratio of 4.7. Temperature-dependent PL spectra and XRD measurements proved that the optoelectronic anisotropy originated from the crystal structure. Zhang and co-workers synthesized lead-free perovskite crystals with 1D structure, presenting outstanding optoelectronic anisotropic performances, as shown in Figure 1.6b.²⁷ The photodetector
fabricated with the crystal exhibits a polarization-sensitive dichroism ratio of 1.31. Besides, the device exhibits high detectivity due to the long-range crystallographic order with minimized grain boundaries. Combining perovskite with other materials with an anisotropic crystal structure is another method to achieve polarization-sensitive detection. Zeng and coworkers fabricated polarization-sensitive photodetectors with PdSe₂/Perovskite Schottky junctions and created an image sensing analysis setup, as shown in Figure 1.6c.²⁸ The detector exhibits a broad detecting band from 200 nm to 1550 nm, a high responsivity of 313 mA/W, and a polarization sensitivity of 6.04.



Figure 1.6 Schematic illustrations of perovskite polarized photodetector based on the anisotropic crystal structure. a) Schematic of FAGPbI₄ structure and polarized light detection based on the crystal.²⁶ b) Schematic of (n-propylammonium)SbBr₅ structure and polarized light detection based on the crystal.²⁷ c) Schematic of the polarized photodetector based on PdSe₂/Perovskite Schottky junctions, and the image sensing analysis setup.²⁸

Linearly polarized perovskite photodetector based on anisotropic morphology

Perovskite nanowires can generally be synthesized using these techniques: capillary force-assisted growth,^{29, 30} space-confined growth,^{31, 32}, oriented force growth,^{33, 34} and nanoimprinting.³⁵⁻³⁸

A liquid exerts capillary force within a narrow space due to the combination of cohesive and adhesive forces. With the guide of capillary force, the perovskite precursor solution can infiltrate the mold with hydrophilic linear arrays, forming nanowires. Feng and coworkers fabricated CsPbBr₃ NWs with the aid of a micropillar-structured template. The device based on the CsPbBr₃ NW achieves a photocurrent polarization ratio of 2.6.²⁹ Pan and coworkers prepared perovskite ink by solving precursors in DMSO, and injected the ink into a two-plate geometry composed of a upper stationary glass blade over a lower nanochannels-containing Si substrate.³⁰ This method can rapidly obtain the continuous large-scale perovskite NWs array.

Space-confined growth is a synthesis technique where the growth of perovskite crystals is restricted within a confined space, such as between two substrates or within a template with limited dimensions. This method aims to control the crystals' morphology, size, and orientation, often resulting in high-quality, uniform, and well-aligned structures. Li and coworkers synthesized a series of quasi-2D perovskite micro-wire arrays by confining the precursor solution in the capillaries formed by a glass substrate 28 and a micro-structured PDMS film.³¹ The device can detect 405 nm polarized light with a polarization ratio 1.7. Jeong and coworkers prepared CsPbBr₃ and CsPbI₃ perovskite NWs via polymer-assisted nanoimprinting by polymer backfilling.³² The as-prepared NWs present outstanding environmental stability at ambient conditions and high temperatures. Zhang and coworkers employed a PDMS template with linear patterns to grow MAPbBr₃ monocrystal thin films with linear arrays on the surface.³⁹ The photodetector based on the prepared thin film presented a polarization–photodetection sensitivity of 2.2.⁴⁰

Oriented force growth is a method for controlling the orientation and alignment of perovskite crystals during their synthesis. This technique leverages external forces or fields to guide the growth direction of the crystals, ensuring that they form with specific crystallographic orientations. Zhou and coworkers synthesized β -CsPbI₃ NWs by dropping the precursor solution onto a 10° titled Si/SiO₂ substrate.³⁴ The NW polarized photodetector demonstrated a photocurrent anisotropy ratio of 2.68, and the flexible device on the PET substrate exhibited a photocurrent anisotropy ratio of 2.17. The device presented excellent flexibility, fantastic folding endurance, and electrical stability. Gao and coworkers prepared MAPbI₃ NWs with a length of up to 2 mm by dropping the precursor solution onto a 10° titled glass substrate.³³ Oleic acid soaking was employed to passivate the NWs. The NW device exhibited low trap density, high carrier mobility, and a photocurrent polarization ratio 1.3.

Nanoimprinting is a versatile and cost-effective technique to create nanoscale patterns or structures perovskites. This process involves mechanically pressing a template with nanoscale features into a material to transfer the pattern. Zhan and coworkers fabricated a butterfly-inspired Hierarchical structure photodetector via nanoimprinting.³⁷ They imprinted the linear pattern of a commercial DVD plate onto the perovskite thin film. With the aid of the linear pattern, absorption of the thin film was improved, and the device presented a photocurrent polarization ratio of 1.6. Song and coworkers achieved moiré-lattices perovskite photodetector by combining two nanoimprinted linear structures.³⁸ A moiré lattice structure is an interference pattern emerging when two periodic structures are overlaid with a slight twist angle or a small lattice mismatch. The moiré photodetector exhibited outstanding photoelectronic performance and is sensitive to linear polarized light. With the different sensitivity to polarized light, a 576pixel image sensor for digital polarization imaging was achieved.



Figure 1.7 Schematic illustrations of NWs Synthesis techniques. a) Capillary forceassisted growth. Solution flow is confined between the micropillar template and the flat substrate. As the solvents evaporate, capillary trailing occurs at the lyophobic–lyophilic boundaries, fabricating CsPbBr₃ NWs.²⁹ b) Space-confined growth. The precursor solution of CsPbX₃ (X = Br or I) with PEO was spin-coated, then the film was

compressed by a PDMS mold with a pattern and annealed. After removing the mold, CsPbX₃ films with nanopattern were obtained.³² c) Oriented force growth. Nanowires grew along with the gradual evaporation of solvent on the flat substrate titled at a slope. SEM image, TEM image, and SAED patterns as synthesized CsPbI3 NWs are presented.³⁴ d) Nanoimprinting. The fabrication process and SEM image of the prepared CsPbI₃ and CsPbBr₃ NWs are exhibited.³⁶

1.5.2 CPL HOIP photodetector

The ability of CPL detection of HOIP photodetectors mainly originates from the different absorption LCP and RCP of chiral perovskite. A more specific mechanism of CPL sensitivity of chiral HOIP will be illustrated in *Mechanism of CPL detection based on chiral HOIPs* in this section later. Chiral HOIP can be constructed in 3D, 2D, quasi-2D, 1D, and nanocrystal structures.

Compared to 2D and 1D chiral HOIPs, there are fewer reports on chiral 3D HOIPs. Ye and co-workers successfully fabricated 3D metal-free organic perovskites with an ABX₃ structure in 2018 (Figure 1.8a).⁴¹ By introducing chiral template organic cations to the A-site, chiral 3D perovskites were obtained. Long and co-workers theoretically predicted that chiral 3D HOIPs could be realized in 2019.⁴² In 2023, Chen and co-workers obtained chiral 3D HOIPs via "heterogeneous chiral nucleation–near

equilibrium autocatalytic growth" as shown in Figure 1.8b.⁴³ In this method, the chirality of the crystal originates from the chiral orientation patterns of the achiral A-site cations and their interaction with the $[PbX_6]^{4-}$ frameworks, and no chiral ligand is required.



Figure 1.8 a) The packing diagram and chemical structure of metal-free organic perovskites MDABCO–NH₄I₃. The crystal can be endowed with chirality with chiral organic cations on A-site.⁴¹ b) Schematics of nucleation and growth of MAPbBr₃ single crystals in homogeneous and heterogeneous solutions, and autocatalytic growth mechanism of chiral MAPbBr₃ crystal.⁴³

2D chiral perovskites generally consist of inorganic layers and chiral organic cations, such as (S/R)-methylbenzylammonium (S/R-MBA) and (S/R)-1-(1naphthyl)ethylamine or (S/R)-1-(2-naphthyl)ethylamine (S/R-NEA). S/R-MBA can 33

form chiral 2D perovskite (S/R-MBA)₂PbI₄. The crystal can be synthesized using the aqueous method.⁴⁴ (S/R-MBA)₂PbI₄ exhibits opposite CD signals⁴⁵ and circularly polarized PL.⁴⁶ Lu and coworkers demonstrated chiral-induced spin selectivity (CISS) effect of (S/R-MBA)₂PbI₄, and proved spin transport in the perovskite can be manipulated via introducing chiral molecules into the spacer layers.⁴⁵ Wang and coworkers fabricated CPL photodetector with (S-MBA)₂PbI₄ and achieved an anisotropy factor of 0.23, as shown in Figure 1.9a.44 S/R-NEA is another ligand that can construct chiral 2D perovskites. Ishii and coworkers synthesized (S/R-NEA)₂PbI₄, and controlled the perovskite dimension from 2D to 1D by adjusting the ratio of Pb²⁺ to NEA⁺ in the precursor solution.⁴⁷ The CPL photodetector fabricated with (S/R-NEA)₂PbI₄ obtained an anisotropy factor of 0.12 (Figure 1.9b). Liu and coworkers prepared chiral perovskite thin films following the stoichiometric ratio of (NEA)₂(MA)_{n-1}Pb_nI_{3n+1} and fabricated photodetectors with the films.⁴⁸ They explored the relationship between the stoichiometric ratio and photoelectronic performance and finally obtained the device with an anisotropy ratio of 0.15 and a responsivity of 15.7 A/W. Combining chiral and achiral ligands is also feasible for preparing chiral 2D perovskites. Zhu and coworkers found that the 1D chiral perovskites (R/S-PPA-NH₃)PbBr₃ can be modified into 2D chiral perovskites (R/S-PPA)EAPbBr₄ by combining ligands R/S-PPA and EA.⁴⁹ They fabricated a CPL photodetector with an impressive dissymmetry factor of responsivity (0.42) based on the 2D chiral perovskite. Zhu and coworkers synthesized chiral ACI-type perovskites (R/S-PPA)PAPbBr4 and 34

observed the structural transition of the crystal (Figure 1.9d).⁵⁰ The self-powered CPL photodetector based on (R-PPA)PAPbBr₄ crystal presented an outstanding anisotropy factor, which increased with the decreasing temperature. Compared to chiral 2D perovskites, chiral quasi-2D perovskites were relatively less reported. Huang and coworkers synthesized chiral quasi-2D perovskites (R/S-β-MPA)₂(MA)Pb₂I₇ and observed bulk photovoltaic effect.⁵¹ Wang and coworkers fabricated (R-β-MPA)₂(MA)Pb₂I₇ crystal into CPL detector (Figure 1.9c).⁵² Their device achieved an anisotropy factor of 0.11 and an outstanding responsivity among chiral 2D perovskite CPL detectors. Besides, they employed antisolvent to prepare pure phase quasi-2D films. The films were fabricated into flexible device with superior mechanical flexibility and durability.



Figure 1.9 2D and quasi-2D chiral perovskites in previous work. a) Photograph, structure schematic, CD spectra, and CPL detection of (S-MBA)₂PbI₄.⁴⁴ b) crystal structure, absorbance spectra, and CD spectra of (S/R-NEA)₂PbI₄.⁴⁷ c) Photograph, structure schematic, CD spectra, and CPL detection of (R-β-MPA)₂(MA)Pb₂I₇.⁵² d) Photograph, structure schematic, CD spectra, and CPL detection of (R-PPA)PAPbBr₄.⁵⁰

Chiral perovskites can also be constructed in a 1D structure. Billing and coworkers synthesized chain-like chiral HOIP (S-C₆H₅C₂H₄NH₃)PbBr₃ in 2003, integrating chiral organic cations with an inorganic lead-bromide framework, resulting in a unique 1D 36

structure.⁵³ Chen and coworkers synthesized 1D chiral perovskite (R/S-MBA)PbI₃, which presents face-sharing [PbI₆]⁴⁻ octahedral chain surrounded by the R/S-MBA⁺ cations.⁵⁴ The as-fabricated CPL detector presents a responsivity of 795 mA/W and an anisotropic factor of 0.1. With studies proceeding on 1D and 2D chiral HOIPs, there is a question: Which 1D structure and 2D structure is the better choice for HOIP CPL photodetector? Based on the investigation on (R/S-PPA-NH₃)PbBr₃ with 1D structure and (R/S-PPA)EAPbBr₄ with 2D structure (Figure 1.9a), Zhu and coworkers speculated that the sensitivity of CPL detection is connected to the charge transport capability. The 2D HOIP possesses inorganic skeletons with higher regularity, thereby being advantageous in spin-dependent carrier transition and collection.⁴⁹ Therefore, chiral HOIPs with 2D structure can be more competitive in CPL detection than 1D chiral HOIPs. They summarized some HOIP CPL photodetectors reported (Figure 1.9b), and found that 2D HOIPs are more likely to present passive CPL distinguishability with a high asymmetry factor.



Figure 1.10 a) Schematic illustration of (R/S-PPA-NH₃)PbBr₃ with 1D structure and (R/S-PPA)EAPbBr₄ with 2D structure. b) Summary of performance of some previously reported HOIP CPL photodetectors.⁴⁹

Chiral HOIPs can also be synthesized as nanocrystals. Compared to CPL photodetectors, chiral HOIP nanocrystals are more frequently applied in CPL illumination.^{55, 56} CPL illumination of chiral HOIP nanocrystals is typically achieved by introducing chiral ligands to the surfaces of nanocrystals. This process induces chirality transfer by coupling the static dipole of the chiral ligands with the transition dipole moment of the nanocrystals.⁵⁶

Mechanism of CPL detection based on chiral HOIPs

In achiral HOIPs, inversion symmetry exists in the crystal structure, and the electronic band is spin-degenerate. The extrema of both conduction and valence band are located at $K_z = 0$, and the exciton is direct with energy minimum occurring at $K_z = 0$, as shown in Figure 1.10a.⁵⁷ When introducing chiral ligands into the structure of a metal halide, its centrally symmetrical structure will be broken, its inversion symmetry will be destroyed, and the original degenerate electron and hole energy states will be separated in k-space (Figure 1.10b-1.10e).



Figure 1.11 a) Band structure of achiral HOIP. b-e) Band structures of chiral HOIP. Schematic illustration of the origin of f) CD and g) CPL.⁵⁷

In chiral HOIPs, both the inversion asymmetry of the crystal structure and the symmetry breaking of surface and interface exist. The noncoplanar arrangement of organic ligands in chiral HOIPs induces a novel spin-orbit coupling (SOC) in the conduction and valence bands, which explains the spin-dependent electrical transport.⁵⁸ The geometry of the chiral organic ligands primarily influences the strength of this chirality-induced SOC. Note that SOC induced by chirality is different from the Rashba effect.⁵⁷ The spin-splitting induced by spin-orbit coupling (SOC) in chiral perovskite materials provides a qualitative explanation for the chiroptical activities of HOIPs, including circular dichroism (CD) and circularly polarized luminescence (CPL). For a photon with wave vector q, left- and right-circularly polarized light generates excitons in different exciton parabolas, with the energy splitting increasing as q increases (Figure 1.10f). The energy at which CD is zero corresponds to the exciton with K=0, forming 39

the basis for CPL photodetectors. The CPL process is essentially the reverse of the CD process: the emission intensities for left- and right-circularly polarized light differ because they originate from excitons in the upper and lower subbands, which have distinct exciton occupations (Figure 1.10g).

1.6 Objectives and outlines of the thesis

1.6.1 Objectives

Relying on the simple preparation process and outstanding optoelectronic properties such as high absorption coefficient, long carrier diffusion length, and tunable band gap, research on HOIP polarized photodetector keeps progressing. Despite those impressive achievements, there are still many barriers worth investigating. For LPL HOIP photodetectors, considering the complicated fabrication process of NWs, it will be good to realize polarization detection without the aid of NWs. Besides, the optoelectronic performance of LPL HOIP photodetectors still requires improvement. Thus, we used quasi-2D HOIPs, which possess outstanding structural stability, controllable phase distribution, and tunable bandgaps, to fabricate the photodetector. We attempted to construct vertical gradient quasi-2D phase distribution in the HOIP film, which is expected to improve the photogenerated charge carrier lifetime and improve photo responsivity of the device. Nanoimprint was operated to form linear nanopatterns aiming to realize linear photodetection.

For CPL HOIP photodetectors, previous works mainly focused on one- 1D and 2D chiral HOIPs, which possess wide bandgap compared with quasi-2D and 3D HOIPs. This is a drawback for photodetector materials because the wide bandgap limits the 40

response wavelength region of the device. Besides, the 1D chain structure and the 2D structure with narrow quantum wells suppress the device's optoelectronic performance. Therefore, we attempted to prepare multiple-phase quasi-2D chiral HOIP films to achieve a device with broadband CPL response and high optoelectronic performance. We found it hard to obtain quasi-2D phases with only chiral molecules S/R-MBA serving as organic spacer ligands, but when PEA and S/R-MBA were used simultaneously. We studied the chiroptical and photoconductive properties of the films with different ligand ratios and attempted to fabricate CPL photodetectors based on the films.

To further study chiral quasi-2D HOIP phases, we fabricated crystals (S/R-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI3_{n+1} crystals with n = 1, 2, and 3. We measured and compared their chiroptical properties. To investigate their photoelectric properties, we fabricated them into CPL photodetectors, compared the photoconductive behaviors of the device, and measured the CPL response of the device.

1.6.2 Outline of thesis

In Chapter 1, we introduce the background of our research and then summarize some basic concepts of light polarization and photodetector; afterward, we introduced HOIPs and reviewed previous works on polarization-sensitive photodetectors based on HOIPs.

Chapter 2 presents the work on nanoimprinted quasi-2D HOIP polarization-sensitive photodetector. We prepared $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$ thin films with vertical gradient phase distribution and nanoscale linear patterns on the surface. The film was then fabricated into LPL-sensitive photodetectors with outstanding optoelectronic performance. Charge carrier dynamics were studied, and the high performance was

explained.

Chapter 3 studies broadband CPL HOIP photodetectors based on (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films. Chiroptical measurements prove the films' wide-region CPL response with suitable ligand ratios. The photoelectric properties of films with different ligand ratios were studied.

In Chapter 4, we synthesized $(S/R-MBA_{0.4}PEA_{0.6})_2MA_{n-1}Pb_nI_{3n+1}$ crystals with n = 1, 2, 3. We compared the optical and photoelectric properties of the three pairs of crystals. The photodetectors fabricated with the chiral crystals were measured under CPL illumination with different wavelengths, and CPL sensitivity was proved.

Chapter 5 summarizes the works on HOIP polarization-sensitive photodetectors and gives a brief future work plan.

Chapter 2 Materials and Characterization Methods

In this chapter, the main chemicals utilized in this thesis are listed, along with three important characterization techniques and their mechanisms.

2.1 Chemicals and reagents

Chemicals	Purity	Company
PEAI	99.5%	Polymer Light Technology Corp.
MAI	99.9%	Polymer Light Technology Corp.
PbI ₂	99.9%	Polymer Light Technology Corp.
BAI	99%	Polymer Light Technology Corp.
i-BAI	99.5%	Polymer Light Technology Corp.
S-MBAI	99%	Polymer Light Technology Corp.
R-MBAI	99%	Polymer Light Technology Corp.
PbO	99.9%	Alfa Aesar
DMF	99.8 %	Sigma-Aldrich
DMSO	anhydrous, 99.9%	Sigma-Aldrich
Hydriodic acid solution	57 wt. %	Sigma-Aldrich

Table 2.1 Main chemicals and reagents utilized in the thesis.

2.2 Main characterization methods for perovskite films and crystals

2.3.1 Transient absorption spectroscopy (TA)

TA is a powerful technique used to analyze the charge carrier dynamics of the sample. In TA measurement, the sample is first excited by a pump-pulsed laser. This pulse excites electrons from the ground state to an excited state. After a controlled delay, a second pulse of laser (probe pulse) is employed to measure the absorption of the sample. The probe pulse passes through the sample, and its intensity is measured after interacting with the excited molecules. Changes in absorption can be detected, indicating how the excited state evolves over time. With signals collected in different delay times between the excitation and probe pulses, TA provides time-resolved information about charge carrier dynamics.

2.3.2 Grazing incidence wide-angle x-ray scattering (GIWAXS)

GIWAXS is a technique used to study the crystal structural properties of thin films. The unique advantage of GIWAXS is that the depth of detection can be controlled by adjusting the incident angle. In measurement, the X-ray beam is directed at a very shallow angle (grazing incidence) onto the sample surface. For GIWAX, the X-ray interacts primarily with the surface or near-surface regions of the sample. As the X-ray penetrates the sample, they are scattered by the atoms in the material. The scattering occurs at various angles, which provides information about the crystal structure of the sample. The scattered X-rays are detected over a wide range of angles, allowing for the analysis of both in-plane and out-of-plane structures. The intensity of the scattered X-rays is recorded as a function of the scattering angle, and the data is typically presented in a 2D scattering pattern, which can be analyzed to extract structural information.

2.3.3 Circular dichroism (CD) spectroscopy

CD Spectroscopy is a technique used to study the chiroptical property of the sample. The mechanism of CD measurement is illustrated in Figure 4.1.¹⁰ CD spectroscopy arises from the differential absorption of right-handed and left-handed circularly polarized lights. During CD measurement, left-handed and right-handed circularly polarized light are alternately produced by a xenon lamp and then pass through the sample. The CD spectrum is obtained by comparing the intensity of the original light with that of the remaining light. The CD signal is always observed at the absorption position.



Figure 2.1 Schematic illustration of CD measurement.¹⁰

Chapter 3 Nanoimprinted Quasi-2D Hybrid Organic-Inorganic Hybrid Perovskite Towards a High-Performance Polarization-Sensitive Photodetector

3.1 Introduction

Polarization-sensitive photodetectors are attracting much attention for their ability to detect the direction and degree of polarization of light, which is valuable in bio-signal detection,⁵⁹ astronomy,⁶⁰ display technology,⁶¹ and military applications.¹³ In recent years, halide perovskites have found promising applications in polarization-sensitive photodetection due to their excellent optoelectronic properties, such as high absorption coefficient,⁷ long carrier diffusion length⁶², and tunable band gap.^{63, 64} In general, the polarization-sensitive perovskite photodetectors (PSPPDs) can be made by using perovskites with intrinsically anisotropic crystal structures or by combining perovskites with other materials that have anisotropic morphology, especially nanowires (NWs).^{44, 69, 70}

Despite these achievements, preparing large-scale and high-quality perovskite crystals with an anisotropy crystal structure is challenging and time-consuming. Preparing perovskite NWs also requires complex techniques like capillary force-assisted growth,^{69, 70} space-confined growth,⁴⁴ and oriented force growth.^{71, 72} Moreover, compared with non-polarized perovskite PDs, optoelectronic performances of PSPPDs are not competitive.⁷³ Attempts were made to prepare PSPPDs with thin films to achieve higher performance. Through the nanoimprinting method, Zhan and coworkers demonstrated a linear-grating structure on MAPbI₃ (MA⁺ = CH₃NH₃⁺) film to realize polarization detection.⁷⁴ With the aid of porous photonic crystals, the perovskite PD exhibited a responsivity of 12.67 A/W under white light. Song and coworkers designed moiré-lattices PDs with dual nanograting based on MAPbI₃ films.⁷⁵ The dual nanograting structure enhanced the PD's light harvesting while achieving polarization detection, and the responsivity was improved up to 15.62 A/W.

Quasi-2D perovskites are a class of perovskite materials that have a layered crystal structure of alternating organic cation layers and an inorganic perovskite layer, unlike traditional 3D perovskites that have a three-dimensional network of corner-sharing octahedra. The layered structure of quasi-2D perovskites provides several advantages, such as outstanding structural stability,^{76, 77} controllable phase distribution⁷⁸, and tunable bandgaps.⁷⁹ The interlayer charge transfer mechanism of quasi-2D perovskites can also enhance carrier diffusion and help mitigate charge trapping and recombination processes, improving charge transport properties.^{80, 81}

We believe there is enormous scope for improving the performance of PSPPD by exploiting the advantages of quasi-2D halide perovskites. Herein, we report a PSPPD based on quasi-2D perovskite film. The thin film of $(PEA)_2MA_2Pb_3I_{10}$ (PEA⁺ = $C_6H_5CH_2CH_2NH_3^+$) was prepared through hot casting. We obtained the perovskite film with gradient phase distribution, in which quasi-2D and three-dimensional (3D) phases separate vertically. Nanoimprinting was employed to introduce a linear pattern on the film's surface. The PSPPD prepared via such a process has advantages in the following two aspects. i) Compared with PSPPD based on NWs and single crystals, the device in this work is prepared through spin-coating and a following nanoimprinting process performed concurrently with annealing, which is more convenient to operate. ii) The phases' spatial separation promotes charge carrier extraction from quasi-2D phases to 3D phases, which highly prolongs carrier lifetime and improves the performance of PSPPD. The device presents a high responsivity of 89.8 A/W and the detectivity of 1.58×10¹² Jones under 0.22 µW/cm² 633 nm illumination. Meanwhile, polarization detection is available in a broadband range, and the maximum anisotropy ratio of photocurrent and photoluminescence reaches 1.68 and 2.05, respectively, at 532 nm illumination.

3.2 Experimental section

Materials: MAI (99.9%), PEAI (99.5%), PbI2 (lead iodide, 99.9%), PEDOT and PCBM

(>99.5%) were purchased from Polymer Light Technology Corp. without further purification. DMF and DMSO were purchased from Sigma-Aldrich.

Materials Synthesis: PEAI, MAI and PbI₂ were dissolved at a stoichiometric ratio of 2:2:3 (following the ratio of (PEA)₂(MA)₂Pb₃I₁₀) in a DMSO/DMF (1:14 volume ratio) mixture, where the total Pb²⁺ molar concentration is 0.5 M. The precursor solutions were then magnetically stirred at 70 °C for 4 hours.

Device Fabrication: The Si/SiO₂ (500 nm thickness for SiO₂) and glass substrates were ultrasonically cleaned sequentially in acetone, isopropyl alcohol, and DI water and then dried with nitrogen gas. Cr (10 nm)/Au (80 nm) electrodes with a channel width and length of 500 and 4 µm were patterned via photolithography and E-beam deposition on the Si/SiO₂ substrates. The substrates were exposed to O₂ plasma for 10 min and preheated at 100 °C for 5 min with a PTFE spin-coating chuck. Then, 60 µL of precursor solution (70 °C preheating for 10 min before use) was dropped onto the preheated substrate, followed by a one-step spin-coating process at 3500 r.p.m. for 40 s. After spin-coating, the film was annealed at 110 °C for 10 min. Nanoimprinting was operated at the same time as annealing. The imprinting master was acquired from commercial DVD-R optical disks. The imprinting pressure was controlled by placing different numbers of metal blocks with a mass of 1.5 kg on the top of the template. With four metal blocks (6 kg in total), a suitable pressure for nanoimprinting can be obtained, and the pressure was calculated to be about 0.26 MPa.

Materials Characterization: The surface morphology of films was measured by an atomic force microscope (Asylum MFP-3D Infinity). An X-ray Diffractometer (Rigaku SmartLab 9kW) was employed to measure X-ray diffraction spectra. Absorption spectra were measured with a UV-Vis-NIR spectrometer (Perkin Elmer). Grazing-incidence wide-angle X-ray scattering (GIWAXS) was measured at the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai, China. The incident angle is 0.1°, and the X-ray energy is 15 keV.

Optical Measurements: For femtosecond optical spectroscopy, the laser source was a Coherent LIBRA regenerative amplifier (150 fs, 1 kHz, 800 nm) seeded by a Coherent Vitesse oscillator (100 fs, 80 MHz). 800 nm wavelength laser pulses were from the regenerative amplifier's output, while 400 nm laser pulses were obtained with a BBO doubling crystal. The emission from the samples was collected at a backscattering angle of 150° by a pair of lenses and into an optical fiber that is coupled to a spectrometer (Acton, Spectra Pro 2500i) to be detected by a charge-coupled device (Princeton Instruments, Pixis 400B). TRPL was collected using an Optronis Optoscope streak camera system with an ultimate temporal resolution of 6 ps. Transient absorption measurements were performed using a Helios setup. Helios acquired the transient dynamics in fs-ns time region (50 fs - 7 ns), which works in a nondegenerate pump-

probe configuration. The pump pulses were generated from an optical parametric amplifier (OPerA Solo) pumped by a 1-kHz regenerative amplifier (Coherent Libra, 800 nm, 50 fs, 4 mJ). A mode lock Ti-sapphire oscillator (Coherent Vitesse, 100 fs, 80MHz) was used to seed the amplifier. The probe pulse was a white light continuum generated by passing the 800 nm fs pulses through a 2 mm sapphire plate for the visible part (420-780 nm). Measurements were carried out in vacuo to reduce any tendency for photo-oxidation.

Optoelectronic Measurements: In ambient conditions, the photoresponse performance under different wavelengths was recorded by a four-probe station (LakeShore CRX-6.5K equipped with Keithley 4200 Semiconductor Characterization System). The illumination sources were CW fiber lasers with wavelengths of 375 nm, 447 nm, 532 nm, 633 nm, and 750 nm. In polarized-light detection, the LEDs with 447 nm, 532 nm, and 633 nm were used as light sources.

3.3 Results

The preparation process of the target sample and a schematic of the anticipated film structure are shown in **Figure 3.1a**. With the hot-casting process followed by an imprinting operation, our perovskite film was expected to possess a vertical gradient 2D/3D phase distribution with the linear nanopattern on the surface (we abbreviated the

target film as L-G-PVK film hereinafter). The hot-casting temperature and the imprinting pressure were discreetly controlled to ensure the pattern of the DVD inner layer was accurately replicated onto the film, while the gradient-phase-distribution-structure produced by hot casting was not damaged. To evaluate the optical properties and optoelectronic performance of L-G-PVK film, we also prepared three other samples for comparison as presented in Figure 3.1b: a control sample with neither linear pattern nor vertical gradient structure (C-PVK, prepared by common spin-coating and annealing process); a film with a linear pattern, but without vertical gradient structure (L-PVK, prepared by common spin-coating with imprinting during annealing process); a film with a linear pattern (G-PVK, prepared by hot-casting, without imprinting during annealing process).



Figure 3.1 a) Schematic illustration of the preparation method of L-G-PVK film. b)

Schematic illustrations of C-PVK film, L-PVK film, G-PVK film, and L-G-PVK film. 52

Figures 3.2a and 3.2b present photographs of the L-G-PVK film prepared on a silicon substrate from two different shooting angles. In Figure 3.2a, the clear visibility of the substrate indicates the film is semitransparent, and the imprinted area in the red dotted box is less transparent than the surrounding area, showing that the imprinted film gets better light absorption ability than the unimprinted area. The colorful reflection observed from another shooting angle in Figure 3.2b is a typical interference phenomenon caused by a linear grating structure ^{82, 83}, just like what we see on the back of a DVD plate. It implies the formation of a linear pattern on the film surface. To further demonstrate that we obtained the linear nanopattern on the film, we used an atomic force microscope (AFM) to measure the film surface morphology. As shown in the AFM height image (Figure 3.2c), it is proved that the regular and clear linear nanopattern was formed. Figure 3.2d presents a height profile extracted from the location of the red arrow in Figure 3.2c. The linear grating with around 0.7 µm in period and approximately 70 nm in height can be observed. This structure matches well with the design of the DVD inner layer (Figure 3.2e,f). Those results prove that the DVD's linear nanograting structure is successfully copied onto the film surface.



Figure 3.2 a,b) Photographs of L-G-PVK film on the silicon substrate from different shooting angles. c) AFM height image of L-G-PVK film surface and d) the height profile corresponding to the red arrow in (c). e) AFM height image of the DVD inner plate and f) the height profile corresponding to the red arrow in (e).

The absorbance spectra of the four films above are shown in Figure 3.3a. All the films exhibit multiphase absorption peaks. The peaks at 517 nm, 569 nm, 610 nm, and 750 nm correspond to the perovskite phase of n = 1, 2, 3, and 3D phases, respectively.⁸⁴ From 525 nm to longer bands, the L-PVK film obtains a higher absorbance than the C-

PVK film, and the L-G-PVK film generally brings a higher absorbance than the G-PVK film, which can be attributed to the enhanced light harvesting resulting from the linear pattern structure. X-ray diffraction (XRD) was employed to characterize the crystal structure of as-synthesized perovskite films, as shown in Figure 3.3b. L-G-PVK and G-PVK film present two significant diffraction peaks at 14.2° and 28.6° corresponding to (111) and (202) crystal planes of quasi-2D phases or (110) and (220) planes of 3D-like phases.⁷⁶ However, in C-PVK film, diffraction peaks of the 3D-like phase are less identifiable than those of L-G-PVK and G-PVK. The higher relative intensities of diffraction peaks at 14.2° and 28.6° in L-G-PVK film and G-PVK film reflect than that in C-PVK film can be attributed to higher 3D-like phase contents or better orientation of quasi-2D phases caused by hot-casting. To better understand the crystal orientation in films under hot-casting preparation, grazing-incidence wide-angle X-ray scattering (GIWAXS) was employed to characterize the crystal structure of G-PVK film (Figure 3.3c) and C-PVK film (Figure 3.3d). With a grazing-incident angle of 0.1°, the G-PVK film exhibits diffraction points sharper in width than the C-PVK film, demonstrating that hot casting enhances crystal orientation. Besides, in the out-of-plane direction, the C-PVK film reveals a diffraction pattern corresponding to (0k0) planes of small-n phases, while those diffraction points do not appear in the G-PVK film. This is because, in G-PVK film, quasi-2D phases tend to adopt a vertical orientation.^{84, 85} The asconfirmed crystal orientation in G-PVK film is desirable because it benefits charge carrier transportation,⁸⁵ which is an important issue for PDs.



Figure 3.3 a) Absorbance spectra and b) XRD patterns of PVK films. GIWAXS pattern of c) G-PVK film and d) C-PVK film.

The hot-casting process can produce a vertical gradient phase distribution, where PVK phases distribute in an order that aligns from low-n value to high-n value from the bottom to the top of the film.^{76, 86} Although there is no consensus on the specific mechanism of this phenomenon, it was speculated to be related to the local molar ratio changing of precursors during the rapid evaporation of the solvent.⁸⁷ The transient absorption (TA) measurements were conducted to examine whether the film's perovskite phases distribute following the vertical gradient phase distribution. A 400 nm femtosecond laser was used to excite the front and back sides (the glass substrate side) of the PVK films, and the induced absorption changes (ΔA) as functions of both

probe wavelength and time were recorded. Figure 3.4a shows the TA spectra at the indicated delay times of the G-PVK film, in which several ground-state bleach (GSB) peaks are observed, which can be assigned to n = 1, 2, 3, 4, and 3D-like phases. The TA spectrum under the front-excitation (0.63 μ J cm⁻²) is dominated by the bleach signals corresponding to 3D phases at 745 nm, whereas the bleach peaks corresponding to quasi-2D phases located in lower bands are weak. In contrast, the spectrum under the back-excitation exhibits strong bleach signals corresponding to n = 1, 2, 3, and 4perovskite phases but no prominent signal of the 3D phase. For comparison, no noticeable difference occurred between the front and back side excited spectra in the C-PVK film (Figure 3.4b). The difference in the TA spectra between back-side and front-side excitations implies that the small-*n* phases are mainly located at the bottom of the G-PVK film, and large-n phases are primarily located at the top. To further confirm the phase distribution originated from the hot casting, photoluminescence (PL) spectra (with 532 nm exciting laser) of L-G-PVK film were measured from both the front side and the back side (Figure 3.4c). The PL intensity corresponding to quasi-2D phases is higher under the back side excitation, while this phenomenon is absent in the C-PVK film (Figure 3.4d). PL and TA measurements proved that the vertical quasi-2D/3D gradient structure was formed via hot casting.



Figure 3.4 TA spectra from the front and back sides of a) G-PVK and b) C-PVK film. PL spectra from the front and back sides of the c) L-G-PVK and d) C-PVK film.

We measured the optoelectronic performances of PDs based on L-G-PVK, L-PVK, G-PVK, and C-PVK (named L-G-PD, L-PD, G-PD, and C-PD, respectively). Cr/Au electrodes were deposited on Si/SiO₂ substrates and patterned by photolithography. Then, perovskite films were prepared on the substrates. **Figure 3.5a** and 3.5b show the current-voltage (IV) curves of L-G-PD, L-PD, G-PD, and C-PD at 8 V bias under light illumination (633 nm, 0.227 mW/cm²) and in dark. The curves exhibit the linear relationship between photocurrents and voltages, demonstrating a good Ohmic contact between perovskite films and Au electrodes. The photocurrent of L-PD (4.27 nA) is around 1.6 times as high as that of C-PD (2.56 nA), which is attributed to the optical absorption enhancement. The photocurrent of G-PD (11.39 nA) is over 4.4 times higher than that of F-PD, indicating the effective spatial separation of photoexcited electron-

hole pairs in the vertical heterojunction structure. The photocurrent of L-G-PD (16.27 nA) is over 6.3 times higher than that of C-PD, which originates from the double enhancement of the grating structure on the film surface and vertical gradient phase distribution. Another important parameter of PDs we get from Figure 3.5a is light on/off ratios, which is the ratio of photocurrent and dark current (abbreviated as I_p and I_d here) of the PD. With 8 V bias voltage, the light on/off ratio of L-G-PD, G-PD, L-PD and F-PD are calculated to be 7.67×10^2 (I_p= 16.27 nA, I_d=21.2 pA), 3.25×10^2 (I_p= 11.39 nA, I_d=35.1 pA), 1.50×10^2 (I_p= 4.27 nA, I_d=28.4 pA) and 0.79×10^2 (I_p=2.56 nA, I_d=32.4 pA), respectively. In Figure 3.5b, *I–V* curves of L-G-PD under illumination (633 nm) with power density from 0.022 to 1.143 mW/cm² with a bias voltage of 8 V show that the photocurrent rises with increasing light power.



Figure 3.5 Photoelectric measurements of perovskite photodetectors. a) *I-V* curves of C-PD, L-PD, G-PD, and L-G-PD under 0.227 mW/cm² 633 nm illumination and b) in dark. c) *I-V* curves of L-G-PD under different light intensities of 633 nm illumination.

Figure 3.6a presents the responsivity (R), given by⁷⁵

$$R = \frac{(I_{ph} - I_{dark})}{PS}$$
 Equation 3.1

where *P* is the light intensity, and *S* is the effective area) of L-G-PD, G-PD, L-PD, and C-PD under the illumination with light power densities changing from 0.226 to 0.486 mW/cm² (corresponding *I-V* curves of L-F-PD, G-PD, L-PD, and C-PD are shown in Figure 3.6c, d, e, and f, respectively). *R* of F-PD, L-PD, G-PD, and L-G-PD increase sequentially under the same light intensity, and for every single PD, the *R* decreases as the light intensity increases, corresponding to the photoconductive device behavior features. Detectivity (*D**), given by⁷⁵

$$D^* = \frac{R\sqrt{S}}{\sqrt{2eI_d}}$$
 Equation 3.2

where *R* is responsivity, *S* is the effective area, *e* is the elementary charge, and I_d is the dark current, another key parameter of a PD that reflects the ability to detect light with weak intensity. As shown in Figure 3.6b, *D** presents the same trend as *R* with changing light power densities from 0.226 to 0.486 mW/cm². The linear dynamic range (LDR) of L-G-PD under 633 nm illumination was calculated by

$$LDR (dB) = 20lg \frac{I_{max}}{I_{min}}$$
Equation 3.3

where I_{max} and I_{min} are the upper and lower limits of the photocurrent in the range where light power density and photocurrent maintain a linear relationship. The photocurrent and the light power density maintain a good linear relationship from 0 to 1.79 mW/cm² illumination, and LDR was calculated to be 7.15 dB.



Figure 3.6 a) R and b) D^* of C-PD, L-PD, G-PD, and L-G-PD under different light intensities of 633 nm illumination. I-V curves of c) L-G-PD, d) G-PD, e) L-PD and f) C-PD under the illumination with light power densities changing from 0.226 to 0.486 mW/cm².

We further measured the light-intensity-dependent performance of L-G-PD with the light intensity changing from 1.14 mW/cm² to 0.22 μ W/cm², as shown in Figure 3.7a.
Corresponding photocurrents under weak light intensities are shown in 3.7b. It was found that *R* reaches the highest value (89.8 A/W) under the light intensity of 0.22 μ W/cm² and *D** presents the same trend as *R* and reaches the highest value of 1.58×10^{12} Jones at 0.22 μ W/cm².



Figure 3.7 a) R and D* of L-G-PD under 633 nm illumination with different light intensities. b) I-V curves with light power densities of 0.22, 2.2 and 22 μ W/cm².

The temporal current of the light switch by the current-time (I–t) curves shown in Figure 3.8a prove that F-PD, L-PD, G-PD, and L-G-PD are stable with repeated light on-off cycles. Figure 3.8b presents the response time of L-G-PD. The rise (τ_r) and decay (τ_d) time of the device are defined as the time taken for the current increase from 10% to 90% of steady-state photocurrent and vice versa. It is shown that τ_r and τ_d are measured to be 17 ms and 15 ms (due to the limitation of the test instrument, shorter time intervals cannot be captured), respectively.



Figure 3.8 a) I-t curves of C-PD, L-PD, G-PD, and L-G-PD under 0.227 mW/cm² 633 nm illumination with 5 V bias. b) Response speed curve of L-G-PD.

The noise currents of C-PD, L-PD, G-PD, and L-G-PD were measured under 4 V bias with no illumination, as shown in Figure 3.9, and we obtained noise spectral densities of each device by Fast Fourier Transform (FFT) from corresponding dark current noises.^{76, 88} Dark current noises from level per unit bands (1 Hz) for C-PD, L-PD, G-PD, and L-G-PD are measured to be 2.07×10^{-2} , 2.30×10^{-2} , 8.89×10^{-2} and 8.26×10^{-2} pA/Hz^{1/2}, respectively. Dark current noises of G-PD and L-G-PD are higher than C-PD and L-PD, but the values are still in the same order of magnitude.



Figure 3.9 Dark current noises of a) L-G-PD, c) G-PD, e) L-PD and g) C-PD, and corresponding noise spectral densities of b) L-G-PD, d) G-PD, f) L-PD and h) C-PD.

Photocurrents of L-G-PD under different power densities of 375 nm, 447 nm, 532 nm, 633 nm, and 750 nm lights were tested (Figure 3.10a-e), and corresponding responsivity

as a function of power density for wavelengths are shown in Figure 3.10f. It can be seen that L-G-PD exhibits broadband photo-response, and in the tested light intensity range, L-G-PD presents the highest responsivity to 633 nm light. External quantum efficiency (EQE) of the PD can be calculated by

$$EQE = \frac{1240 \times R(A/W)}{\lambda(nm)}$$
 Equation 3.4

where R is the responsivity, λ is the wavelength of light. From Figure 3.10f, EQE of L-G-PD were calculated to be 742% (633 nm, 0.227 mW/cm²), 607% (750 nm, 0.105 mW/cm²), 206% (532 nm, 1.001 mW/cm²), 289% (447 nm, 0.435 mW/cm²), and 186% (375 nm, 0.552 mW/cm²).



Figure 3.10 I-V curves of L-G-PD under different power densities of a) 375 nm, b) 447 nm, c) 532 nm, d) 633 nm and e) 750 nm lights. f) The calculated responsivity as a function of light power density.

There is a controversial point that needs to be analyzed. Insulating ligands in quasi-2D perovskites hinder interlayer charge transport, which impedes device performance. Then, is the higher content of MAPbI₃ or the vertical gradient structure the one that causes higher responsivity of G-PD than C-PD? To clarify this concern, we prepared PDs of MAPbI₃ with the same device structure as C-PD. Figure 3.11a presents *I-V* curves of MAPbI₃ under several light intensities, and Figure 3.11b presents *R* at 8 V calculated from the *I-V* curves. The responsivity of PDs made of pure MAPbI₃ is still lower than G-PD. So, it can be proved that the higher responsivity of L-G-PD and G-PD than L-PD and C-PD is mainly caused by the gradient structure rather than the higher MAPbI₃ content.



Figure 3.11 a) *I-V* curves of MAPbI₃ photodetector under 633 nm illumination. b) R calculated from (a).

To gain insights into the photo-physics of perovskite thin films, the charge carrier dynamics in quasi-2D perovskite films were studied by transient absorption (TA) spectroscopy. TA spectra at selected delay times of C-PVK film and G-PVK film are presented in Figures 3.12a and 3.12b, respectively. The control perovskite C-PVK film features three pronounced ground-state bleach (GSB) peaks at 567, 609, and 644 nm corresponding to n = 2, 3, and 4 phases in the TA spectra. In stark contrast to C-PVK perovskite, TA spectra of G-PVK depict weaker intensity of PB peaks at small-*n* phases and a distinct photobleaching (PB) peak of 3D-like phases at 746 nm. The TA kinetics profiles of G-PVK film and C-PVK film were recorded at the corresponding peak positions, as shown in Figures 3.12c and 3.12d, respectively. The ultrafast decay component for the control film exhibits time constants 0.29 ps (n = 2) and 0.28 ps (n = 3)(Table 3.1), which is closely matched with the formation time constant of 0.44 ps for GSB at 668 nm. Note that the bleaching signal at n = 2 and n = 3 persists after a long excitation time, suggesting that there are carriers accumulated in the n = 2 and 3 phases in particular, resulting from the incomplete charge transfer between the different phases. Moreover, the GSB peak at 640 nm (n = 4) shows no charge transfer to the high energy phase but recombination itself. For $n \le 5$, phases of G-PVK perovskite are dominated by the fast decay component and in good agreement with the rapid formation time of 3D-like phases, according to the fitting parameters (Table 3.2). In the G-PVK perovskite film, the fast decay time for the n = 2, n = 3, n = 4, and n = 5 phases is 67

estimated to be 0.21, 0.33 ps, 0.33 and 0.59, respectively (Fig. 4d), while the buildup time of 0.91 ps for the 3D-like phase. These results demonstrate that charge carrier transfer (most likely the electrons in our case) occurs inside the reconstructed phases, enabling more efficient energy transfer from small-*n* phases to large-*n* phases.⁸¹ Photogenerated electrons are mainly assembled in 3D-like phases on top of the film, and the carriers have a specific spatial distribution. In this case, those trapped carriers can produce an additional electric field like gate voltage, which promotes carrier transport and extraction in PDs.⁸⁹



Figure 3.12 TA spectra at various delay times of the a) C-PVK and b) G-PVK film and corresponding kinetics profiles probed at different wavelengths of c) C-PVK and d) G-PVK film.

Table 3.1. Fitting parameters for TA curves of C-PVK film.

	т _{rise} [ps]	a ₁	т ₁ [ps]	a ₂	т ₂ [ps]	a₃	т ₃ [ps]	a₄	т ₄ [ps]
568 nm	0.20	-0.41	0.29	-0.26	15.1	-0.16	186	-0.08	4442
609 nm	0.20	-0.51	0.28	-0.25	15.3	-0.20	159	-0.08	2784
640 nm	0.16	-0.38	3.09	-0.43	62.3	-0.12	902		
668 nm	0.44	-0.69	55.5	-0.29	559	-0.02	>7 ns		

Table 3.2. Fitting parameters for TA curves of G-PVK film.

	T _{rise} [ps]	a ₁	т ₁ [ps]	a ₂	т ₂ [ps]	a ₃	т ₃ [ps]
568 nm	0.20	-0.90	0.21	-0.04	505	0.06	7884
609 nm	0.18	-0.95	0.33	-0.05	43.0		
640 nm	0.19	-0.92	0.33	-0.08	16.5		
668 nm	0.42	-0.91	0.59	-0.10	64.4		
746nm	0.92	-0.59	272	-0.41	4192		

Furthermore, time-resolved photoluminescence spectra (TRPL, excited from the perovskite side) were employed to verify the promotion of carrier transport properties in these perovskite thin films (fitting parameters in Tables 3.3 and 3.4). By analyzing PL emission at 750 nm, as shown in Figure 3.13a, we found that the carrier decay lifetime of G-PVK film (142 ns) is prolonged compared to that of C-PVK film (95 ns). Besides, with the aid of a top PCBM layer and a sub-PEDOT layer, the electron/hole diffusion length of G-PVK film and C-PVK film were also estimated according to a 1D

carrier diffusion model:90

$$L_D \approx \frac{2d\sqrt{2\left(\frac{\tau}{\tau_{hetero}} - 1\right)}}{\pi}$$
 Equation 3.4

where τ is the PL lifetime of the bare film, τ_{hetero} is the PL lifetime of the chargetransport layer/perovskite film, *d* is the thickness of the perovskite film (the thicknesses of C-PVK and G-PVK film are measured to be 300 nm and 890 nm, respectively). From C-PVK film, the electron and hole diffusion lengths were calculated to be 484 nm and 122 nm, respectively, while the electron and hole diffusion lengths were prolonged to 893 to 291 nm in G-PVK film (Figure 3.13b). The corresponding TRPL spectra of G-PVK and C-PVK film with PEDOT sublayer/PCBM upper layer are also shown in Figures 3.13c and 3.13d. The improved carrier transport properties in a vertical gradient structure within the G-PVK film benefit the performance consistent with the PD device results.



Figure 3.13 a) TRPL spectra at the emission center for the G-PVK, G-PVK/PEDOT, 70

and G-PVK/PCBM thin films. b) Electron/hole diffusion length of G-PVK film and C-PVK film. Carrier diffusion lengths were estimated according to a 1D carrier diffusion model. TRPL spectra of c) G-PVK and d) C-PVK film with PEDOT sublayer/PCBM upper layer.

	A ₁	T ₁	A ₂	T ₂	Tave	Thickness	L _d
		[ns]		[ns]		[nm]	[nm]
C-PVK	1	95			95	300	
C-PVK+PEDOT	0.71	54	0.29	140	78.9		122
C-PVK+PCBM	1	44			44		291

Table 3.3. Fitting parameters for TRPL curves of C-PVK film.

	Table 3.4.	Fitting parameters	for TRPL curves of	G-PVK film
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	A 1	T ₁	A ₂	T ₂	Tave	Thickness	L _d
		[ns]		[ns]	[ns]	[nm]	[nm]
G-PVK	1	142			142	890	
G-PVK+PEDOT	0.38	42	0.62	142	104		484
G-PVK+PCBM	0.63	42	0.27	137	63.45		893

Besides promoting optoelectronic performances, another advantage of the linear nanopattern is endowing the device with the ability to detect polarization-sensitive light.^{74, 75, 91} This property was explained by the dielectric contrast between linear structure (or NWs) and the surrounding environment and the resulting polarizationdependent optical absorbance.92 We measured the PL of L-G-PVK film at room temperature with 532 nm and 633 nm linearly polarized exciting laser, respectively. The polarization angle was defined as 0° when the polarization direction is parallel to the nanograting lines and 90° when the polarization direction is perpendicular to the nanograting lines. When the polarization angle changed from 0° to 90°, as shown in Figure 3.14a (532 nm excitation) and Figure 3.14b (633 nm excitation), the intensity of the PL peak declined. When continuing to change the polarization angle from 90° to 180°, the PL peak intensity rose back. Figure 3.14c exhibits PL intensities at 757 nm (532 nm excitation) and PL intensities at 761 nm (633 nm excitation) as a function of the polarization angle. The trends of PL intensity for the L-G-PVK film are presented, and the polarization ratios (the PL intensity ratio between 0° and 90°) are calculated to be 2.05 for 532 nm excitation and 1.70 for 633 nm excitation. However, for G-PVK, the PL intensity did not change under the same operation (Figure 3.14c, 3.14d, and 3.14e).



Figure 3.14 PL spectra of the L-G-PVK film with polarization angles of 0° to 90° under a) 532 nm and b) 633 nm polarized exciting sources. PL spectra of the G-PVK film with polarization angles of 0° to 180° under c) 532 nm and d) 633 nm polarized exciting sources. e) PL intensity at 750 nm as a function of polarization angle.

Furthermore, we measured the polarization dependence of the photocurrent of L-G-PD.

The polarized lights were produced by LED illuminations with the 447, 532 and 633 nm wavelength penetrating a linear polarizer, as shown in Figure 3.15a. As shown in Figure 3.15b-3.15d, the photocurrent of the L-G-PD device decreases with the polarization angle gradually declining from 0° to 90°. The polar plots of photocurrents with 4 V bias are shown in Figure 3.15e. The value of photocurrents with 4 V bias rose and fell when the polarization angle changed from 0° to 180°. The peak-to-valley ratio of photocurrent calculated from polarization angles of 0° and 90° were estimated to be 1.64, 1.68, and 1.60 for 447, 532, and 633 nm illumination, respectively, which demonstrates a high polarization sensitivity of L-G-PD. Time-resolved photo response measurements were performed under 4 V bias with 447, 532, and 633 nm illumination, as shown in Figure 3.15f. The polarization angle was gradually changed from 0° to 180° (with every time the illumination switched on and off, the polarizer was rotated 15°). It was shown that the photocurrent first decayed and then rose in this process. Performance parameters of our L-G-PD and several other reported perovskite polarization-sensitive photodetectors are compared in Table 3.5. The responsivity, detectivity, response time, and anisotropy ratio are higher than most previously reported perovskite polarization-sensitive photodetectors.



Figure 3.15 a) Schematic illustration of polarization-sensitive photodetection of L-G-PD. I-V curves under polarized illuminations with wavelengths of b) 447, c) 532 and d) 633 nm with polarization angle from 0° to 90° . g) Photocurrent dependence from 0° to 180° polarization angle. f) Time-resolved photocurrent measurement with polarization angle changing from 0° to 180° with 447, 532, and 633 nm illumination.

Table 3.5. Detailed parameters for comparison with some previously reported

Active lover	Preparation	Responsivity	Detectivity	Rise/decay	Anisotropy	Pofe
Active layer	method	[A/W]	[Jones]	time	ratio	Reis.
	imprinting	00.0	12	<17 ms, 15	0.05 4.00	This
(PEA)2(IVIA)n-1PDnI3n+1	imprinting	09.0	1.58×10	ms	2.05, 1.06	work
	Space-	4.05	13	-0.1 mo	1 0	[00]
	confined	4.95	2×10	<0.11115	1.2	[၁၁]
MARbl, this film	imprinting	10.67	13	67, 21 ms=	1.6	[37]
	Imprinting	12.07	3.22×10	ms	1.0	[37]
	Capillary					
$CsPbBr_3 NWs$	force	5.49	/	95/40 ms	1.24	[30]
	assisted					
	Oriented-					[34]
CsPbl ₃ NWs	force-	0.754	¹⁰ 3.46×10	/	2.68	
	assisted					
MAPbBr ₃	Sapce-	0.000	10	0.4	2.2	[40]
Single crystal	confined	0.008	1.08×10	0.15		
(iBA) ₂ MAPb ₂ Cl ₇ single	Solution	-5	9 2.2×10	1	2.5	[14]
crystal	growth	6.78×10		1		
MAPbl ₃ nanoribbon	Space-	-2	8.21×10	27.2, 26.2		10.41
arrays	confined	3.89×10		ms	1.44	[94]
(BPA) ₂ PbBr ₄ single	Solution	-4	7	07/00	6.08	[95]
crystal	growth	1×10	10	27/30 µs		
(iPA) ₂ CsAgBiBr ₇	Solution	,			1.35	[96]
single crystal	growth	1	/	200/400 µs		
(iBA) ₂ PbI ₄ /PdSe ₂	,		10		1.56	[28]
heterojunction	/	0.56	1.23×10	233/166 ms		
(n-propylammonium)	0.1.7			45/68 µs		[97]
(methylammonium)	Solution	/	9 1.1×10		1.31	
SbBr ₅	growth					
	chemical			000.0		[98]
BaTiS₃ NWs	vapor	1.22	3.8×10	263.8 ms,	1.09	
	transport			180.5 MS		

polarization-sensitive perovskite photodetectors

3.4 Conclusion

In summary, a polarization-sensitive perovskite photodetector (PSPPD) based on quasi-2D perovskite thin film was achieved with a polarization sensitivity of 1.68, responsivity of 89.8 A/W and detectivity of 1.5×10^{12} Jones. Polarization detection is based on a nanoimprinted linear pattern and is available in a broadband range. Meanwhile, the linear pattern on the surface enhances the ability to harvest light, thereby improving the photodetector performance. Transient absorption (TA) and photoluminescence spectra demonstrated the spatial separation of 2D and 3D-like phases caused by hot-casting. The charge carrier dynamics studied from TA spectra reveal the efficient charge funneling from small-n phases gathered at the bottom of the film to the top high-n phases, forming a photogating structure. This behavior of the charge carrier results in a long carrier lifetime and leads to the high responsivity of the photodetector. Our trial confirmed the feasibility of fabricating PSPPD on quasi-2D perovskite thin film. The research should facilitate the development of highperformance polarization-sensitive photodetectors.

Chapter 4 Chiral Quasi-2D Perovskite Towards Circular-Polarization-Sensitive Photodetector Over Wide Wavelength Range

4.1 Introduction

Organic-inorganic hybrid perovskites (HOIPs) attracted much attention due to their outstanding light-harvesting ability, long carrier diffusion length, and tunable band gap. Research on HOIP has led to impressive development in solar cells, light-emitting diodes, transistors, and photodetectors (PDs). Circularly polarized light (CPL) detection is important in OHIP PDs. Chiral HOIP, which exhibits CPL-sensitive optical absorption and efficient charge carrier transport, has been proven to be a promising candidate for CPL detection. A common method to construct chiral HOIPs involves incorporating chiral ligands into the lattice. For example, with introducing chiral organic molecules (S/R)-methylbenzylammonium (S/R-MBA) and (S/R)-1-(1naphthyl)ethylamine or (S/R)-1-(2-naphthyl)ethylamine (S/R-NEA), the chiral perovskites (S/R-MBA)₂PbI₄, (S/R-NEA)₂PbI₄, S/R-MBAPbI₃, and S/R-NEAPbI₃ can be synthesized and fabricated into CPL PD. Under the left-handed circular polarized (LCP) and the right-handed circular polarized (RCP) illumination, the chiral HOIP PDs present distinct photocurrents and responsivities.

The chirality of chiral HOIPs is considered to have originated from the asymmetry that transferred from the chiral ligands to the perovskite octahedral frameworks.^{57, 99} Therefore, chiroptical properties of OIHPs, such as circular dichroism (CD) and CPL illumination, always occur near the excitonic absorption band of the perovskite and highly correlate with the band gap of HOIPs.¹⁰⁰ Current research on OIHP-CPL PDs has mainly focused on one-dimensional (1D) and two-dimensional (2D) chiral HOIPs characterized by relatively wide bandgap. However, for PDs, a material with tunable bandgap and broad response region is preferred. Some efforts have been made to explore bandgap-tunable chiral HOIPs. Ahn and coworkers controlled the ratio of halide anions in HOIP to modulate the bandgap effectively.¹⁰⁰ Through the gradual substitution of iodine with bromide, the CD signal of HOIP exhibited a shift towards the shorter-wavelength region. Yao and coworkers fabricated CPL PDs using lead-tin mixed HOIP films.¹⁰¹ Compared to pure lead HOIP films, the lead-tin mixed HOIP film can present a wider absorption and CD region. Despite the advantages offered by these studies, certain limitations remain. The Iodine-bromide mixed HOIPs cannot realize broad-band CD in a single film. Besides, substituting iodine with bromide in HOIPs may hinder the photo response in optoelectronic devices. The lead-tin mixed HOIPs encounter the issue of weakened CD signal with increasing tin content in the film, and the stability of tin-containing HOIPs is also a potential concern.

In Chapter 3, we fabricated (PEA)₂MA₂Pb₃I₁₀ (PEA⁺ = $C_6H_5CH_2CH_2NH_3^+$) films with 79

multiple quasi-2D phases distribution. The film presents a broad absorption region, and the PD based on (PEA)₂MA₂Pb₃I₁₀ film exhibits broadband photo-response. Inspired by these findings, in this work, we attempt to prepare chiral HOIP films with multiple quasi-2D phase distributions to achieve broadband CPL PD. Chiral ligands S/R-MBA were employed to introduce chirality into the HOIP films. It was challenging to obtain quasi-2D phases in (S-MBA)₂MA_{n-1P}b_nI_{3n+1} films. However, when PEA and S/R-MBA were simultaneously present in the film, (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films contained multiple quasi-2D phases and showed CD signals in a wide region. We investigated the optoelectronic performance of PDs based on (S/R-MBAxPEA1x)2MA2Pb3I10 films with varying ligand ratios and fabricated a CPL PD with (R-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀ film. The resulting PD demonstrated broadband photoresponse and exhibited a high responsivity of 1.07 A/W under 0.742mW/cm² 447 nm illumination. Besides, the PD exhibited CPL sensitivity in a wide wavelength range. The anisotropy factor of photocurrents (g_{Iph}) with 447 nm, 532 nm, and 633 nm CPL illumination was measured to be 0.11, 0.19, and 0.10, respectively.

4.2 Experimental section

Materials: MAI (99.9%), PEAI (99.5%), BAI (99%), i-BAI (99.5%), S-MBAI (99%), R-MBAI (99%), and PbI₂ (lead iodide, 99.9%) were purchased from Polymer Light Technology Corp. without further purification. DMF and DMSO were purchased from *Materials Synthesis:* Precursors were dissolved following the stoichiometric ratio of chemical formulars (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀, (S/R-MBA_xBA_{1-x})₂MA₂Pb₃I₁₀, and (S/R-MBA_xi-BA_{1-x})₂MA₂Pb₃I₁₀ in a DMSO/DMF (1:14 volume ratio) mixture. The total Pb²⁺ molar concentration is 0.3 M. The precursor solutions were then magnetically stirred at 70 °C for 4 hours.

Thin Films Preparation and Device Fabrication: The Si/SiO₂ (500 nm thickness for SiO₂) and glass substrates were ultrasonically cleaned sequentially in acetone, isopropyl alcohol, and DI water and then dried with nitrogen gas. Cr (10 nm)/Au (80 nm) electrodes with a channel width and length of 500 and 4 μ m were patterned via photolithography and E-beam deposition on the Si/SiO₂ substrates. The substrates were exposed to O₂ plasma for 10 min. 60 μ L perovskite precursor solutions were dropped onto the substrates, spin-coated at a speed of 3500 rpm for 60 s on substrates, and annealed at 110 °C for 10 mins. For hot casting samples, the precursors solution was heated at 70 °C for 10 mins, the PTFE spin-coating chuck and substrates was preheated at the certain temperature for 10 mins, and operated spin-coating process.

Materials Characterization: The X-ray Diffractometer (Rigaku SmartLab 9kW) was employed to measure X-ray diffraction spectra. Absorption spectra were measured with ⁸¹ a UV-Vis-NIR spectrometer (Perkin Elmer). Grazing-incidence wide-angle X-ray scattering (GIWAXS, Xenocs Xeuss 2.0) was measured with an incident angle is 0.5°.

Chiroptical measurement: Circular dichroism (CD) spectra were characterized by the CD spectrometer (JASCO J-1500 Easton, MD) at room temperature.

Optoelectronic Measurements: The photoresponse performance under different wavelength lights was recorded by a four-probe station (LakeShore CRX-6.5K equipped with Keithley 4200 Semiconductor Characterization System) in ambient conditions. The illumination sources were CW fiber lasers with wavelengths of 375 nm, 447 nm, 532 nm, 633 nm, and 750 nm. For circularly polarized light (CPL) detection, the lasers generated the CPL with 447 nm, 532 nm, and 633 nm, sequentially penetrating a linear polarizer and a quarter-wave plate.

4.3 Results

For perovskites with S/R-MBA⁺ serving as chiral ligands, previous works mainly focus on one-dimensional (1D) and two-dimensional (2D) phases, namely (R/S-MBA)PbI₃ and (R/S-MBA)₂PbI₄.^{44, 46, 54, 102-104} However, quasi-2D phases (also known as Ruddlesden–Popper phases) of S/R-MBA⁺-ligand-perovskite was hardly studied. According to previous research, when adding MA⁺ into S/R-MBA⁺-ligand-perovskite thin films, no obvious spin-polarized absorption peaks from quasi-2D phases can be observed, and circular dichroism (CD) signals come mainly from 2D phases.¹⁰⁵ To explore the feasibility of synthesizing quasi-2D phases perovskite with S/R-MBA⁺ ligands, we prepared thin films via spin-coating following the formula (S-MBA)₂MA_n-₁Pb_nI_{3n+1}. Figure 4.1a presents films' UV-vis absorption spectra with stoichiometric ratios of n = 2, 3, and 4. All the films present absorption peaks at around 500 nm corresponding to $(S-MBA)_2PbI_4$ (n = 1) and around 750 nm corresponding to the 3D phase ($n = \infty$). However, absorption peaks of quasi-2D phases were not presented. Xray diffraction (XRD) was employed to analyze further the phase distribution of n = 2, 3, and 4 films (Figure 4.1b). The films exhibit diffraction peaks at 14.2° and 28.6° corresponding (110) and (220) planes of 3D. Besides, diffraction peaks located at 6.1°, 12.2°, 18.4°, and 24.6° correspond to (002), (004), (006), and (008) planes of (S-MBA)₂PbI₄ phase, respectively.¹⁰⁶ The signals of quasi-2D phases, like the results in UV-vis absorption spectra, were not found. Hot-casting is a technique available for controlling the phase distribution of perovskite films.^{107, 108} We performed hot-casting with 100 °C and 120 °C heating temperatures to prepare (S-MBA)₂MA₂Pb₃I₁₀ thin films. Absorption spectra (Figure 4.1a) and XRD patterns (Figure 4.1b) of as-prepared hotcasting films still exhibit only 2D and 3D phases but no signals of quasi-2D phase. These results indicate that obtaining perovskite films with quasi-2D phases with R-MBA+ ligands might be difficult via a common spin-coating method. It is significantly different from common achiral ligands such as BA⁺ and PEA⁺, for which perovskite 83

thin films present multiple quasi-2D phases distribution.^{107, 108}



Figure 4.1 a) Absorbance spectra and b) XRD patterns of PVK films with different stoichiometric ratios and hot casting temperatures.

It is worth noting that during our attempt at preparing (S-MBA)₂MA₂Pb₃I₁₀ thin films with hot-casting, we found that hot casting significantly improves circular dichroism (CD) signals of the thin film, although it cannot generate quasi-2D phase. The CD measurement is a powerful method to investigate the chirality of chemicals. When the sample has different absorbance to the lift/right-handed circular polarized light in a particular wavelength band, the CD spectra exhibit signals at the corresponding locations, known as the "Cotton effect". The cotton effect always occurs at the absorption position due to the CD spectrum, which can be obtained by comparing the original and remaining light intensity.¹⁰ We measured absorption and CD spectra of (S-MBA)₂MA₂Pb₃I₁₀ films prepared with different hot-casting temperatures from 80 °C to 160 °C. The films with all the hot-casting temperatures and the film prepared via the common spin coating method (referred to as RT in Figure 4.2) present the characteristic absorption peaks at around 500 nm corresponding to $(S-MBA)_2PbI_4$ (Figure 4.2a). The films exhibited CD signals at around 500 nm, which first rose and then declined with the increase in hot-casting temperature, as shown in Figure 4.2b. The CD signal reaches the highest value, 210, with a hot-casting temperature of 120 °C. The anisotropy factor of CD (g_{CD}) can be calculated by the following equation:⁵⁴

$$g_{CD} = \frac{CD \ [mdeg]}{32980 \times absorbance}$$
Equation 4.1

The g_{cd} value presents the same trend as CD with increasing hot-casting temperature from 80 °C to 160 °C, reaching the highest value (0.0023) at 120 °C (Figure 4.2c).



Figure 4.2 a) Absorbance spectra, b) CD spectra, and c) corresponding g_{CD} spectra of (S-MBA)₂PbI₄ films with different hot casting temperatures.

As an organic ligand for perovskite, PEA has the same molecular formula and functional groups as S/R-MBA although it is achiral because the amino group is located at the further carbon atom from the benzene ring. The molecular structures of S-MBA, R-MBA, and PEA are compared in Figure 4.3a. Our previous work prepared (PEA)₂MA₂Pb₃I₁₀ thin films with multiple quasi-2D phase distributions.¹⁰⁸ We ⁸⁵

speculate we can replace a part of PEA⁺ with S/R-MBA⁺, embedding chiral ligands into quasi-2D phases. We fabricated perovskite thin films following the formula (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ via hot-casting with 120 °C heating temperature. With the value of x increases, more PEA⁺ were replaced by S/R-MBA⁺. To investigate the change of crystal structures with increasing the ratio of chiral ligands in (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films, we employed XRD to characterize (S-MBA_xPEA₁₋ $_{x}_{2}MA_{2}Pb_{3}I_{10}$ films with x = 0, 0.2, 0.4, 0.6, 0.8, and 1 as shown in Figure 4.3b. When x = 1, the film contains only the S-MBA ligand and no PEA ligand. Consistent with the result in Figure 4.2b, the XRD pattern only presents the diffraction peaks of (S-MBA)₂PbI₄ and 3D phase. When x declines to 0.8 and 0.6, the diffraction peaks of (S-MBA)₂PbI₄ and 3D phase still exist. Besides, the multiple diffraction peaks indicate complicated quasi-2D phase distribution in the films.⁸⁶ When x declines to 0.4 and 0.2, the diffraction peaks of (S-MBA)₂PbI₄ disappear. The XRD patterns present diffraction peaks of the 3D phase and multiple quasi-2D phases. When x declines to 0, the film contains no chiral ligand. The diffraction peaks in the XRD pattern correspond to the 3D and low-dimensional phases with the PEA ligand. We employed grazing-incidence wide-angle X-ray scattering (GIWAXS) to compare further the crystal structure of films with x = 0 and x = 0.4. As shown in Figure 4.3c, with a grazing-incident angle of 0.5° , (S-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀ sharper diffraction presents points than S-MBA₂MA₂Pb₃I₁₀ film, which indicates introducing PEA ligand might enhance the crystal orientation of S-MBA2MA2Pb3I10 film. In the in-plane direction, (S/R-86

 $MBA_{0.4}PEA_{0.6})_2MA_2Pb_3I_{10}$ presents denser diffraction points than S-MBA_2MA_2Pb_3I_{10} film at around q = 2 Å⁻¹, revealing more complicated phase distribution in (S/R-MBA_0.4PEA_{0.6})_2MA_2Pb_3I_{10} film.



Figure 4.3 a) Molecular structures of S-MBA, R-MBA, and PEA. b) XRD patterns of (S-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films. c) GIWAXS patterns of S-MBA₂MA₂Pb₃I₁₀ film and (S-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀ film.

We measured absorbance spectra (Figure 4.4a) and CD spectra (Figure 4.4b) of (S/R- $MBA_xPEA_{1-x})_2MA_2Pb_3I_{10}$ films with ligands content changing from x=0 to x=1. When x=0, the absorbance spectrum shows multiple peaks. The peaks located at 513 nm, 565 nm, and 612 nm correspond to n=1, n=2, and n=3 phases of PEA_2MA_{n-1}Pb_nI_{3n+1},

respectively. With the x value increasing to 0.2, 0.4, 0.6, and 0.8, the absorbance spectra still present three peaks at locations similar to when x=0. When x=1, the peaks located at 505 nm correspond to the 2D phases S/R-MBA₂PbI₄. The CD spectrum shows no obvious signal when x=0 due to no chiral ligands in the film. CD spectra of x = 0.2show slight fluctuation in a band range from 400 nm to 600 nm, but the signal is weak. When the x value reaches 0.4, the CD spectra present two clear opposite curves ranging from around 430 nm to 740 nm in a broadband range. The CD signals in both S- and R- films exhibit three peaks that match well with peaks in absorbance spectra, indicating multiple chiral phases exist in the films. With increasing x to 0.6 and 0.8, the CD signals cover a wide band with multiple peaks. When x reaches 1, the range of CD signals shrinks to narrow bands at around 505 nm and 406 nm, which is the characteristic CD spectra of (S/R-MBA)₂PbI₄.^{103, 106} The corresponding g_{CD} of CD spectra above was calculated in Figure 4.4c. It showed that g_{CD} of (S/R-MBA_xPEA₁- $_{x}$)₂MA₂Pb₃I₁₀ films was at 10⁻³ level. The CD signal range of those perovskite films differs from the CD signals of the S/R-MBA located at around 259 nm,⁵⁴ which demonstrates the chirality of chiral organic cations were transferred to the electronic states of perovskite frameworks.¹⁰⁹ The multiple CD signals of films with x = 0.4, 0.6, and 0.8 reveal that the chiral ligands S/R-MBA embed into perovskite phases PEA₂MA_{n-1}Pb_nI_{3n+1} and transferred chirality to quasi-2D phases. Meanwhile, CD spectra of (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films above demonstrate that when the x value is between 0.4 to 0.8, perovskite films exhibit a wide band chiroptical response 88





Figure 4.4 a) Absorbance spectra, b) CD spectra, and c) corresponding g_{CD} spectra of $(S/R-MBA_xPEA_{1-x})_2MA_2Pb_3I_{10}$ films with different ratios of ligands.

Besides PEA⁺, we tried combining S/R-MBA and other ligands (BA, i-BA) to form quasi-2D chiral perovskites. We prepared (S-MBA_xBA_{1-x})₂MA₂Pb₃I₁₀ and (S-MBA_xiBA_{1-x})₂MA₂Pb₃I₁₀ films with different x values via the same process as we prepared (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films. The absorbance and CD spectra of (S- $MBA_xBA_{1-x})_2MA_2Pb_3I_{10}$ films are shown in Figures 4.5a and 4.5b. With increasing x from 0 to 1, what is different to $(S/R-MBA_xPEA_{1-x})_2MA_2Pb_3I_{10}$ is when x=0.2, 0.4, and 0.6, CD spectra present no obvious signals, although the absorbance spectra contain multiple peaks corresponding to low-n phases. When x = 0.8 and 1, the characteristic signal of (S-MBA)₂PbI₄ presents in CD spectra. The absorbance and CD spectra of (S-MBA_xi-BA_{1-x})₂MA₂Pb₃I₁₀ films are shown in Figures 4.5c and 4.5d. The absorbance spectra present multiple peaks when increasing x from 0 to 0.8. The CD spectra exhibit only the characteristic signal of (S-MBA)₂PbI₄ when x reaches or exceeds 0.4, but no other peaks. The CD measurements of (S-MBAxBA1-x)2MA2Pb3I10 and (S-MBAxi-BA1x)2MA2Pb3I10 films indicate that introducing S/R-MBA to quai-2D perovskite phases constructed by other organic ligands is not a universal method to obtain chiral quasi-2D perovskites, although it is effective in (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ system.



Figure 4.5 Absorbance spectra of a) (S-MBA_xBA_{1-x})₂MA₂Pb₃I₁₀ films and b) (S-MBA_xi-BA_{1-x})₂MA₂Pb₃I₁₀ films. CD spectra of c) (S-MBA_xBA_{1-x})₂MA₂Pb₃I₁₀ films and d) (S-MBA_xi-BA_{1-x})₂MA₂Pb₃I₁₀ films.

Semiconducting behaviors are prerequisites for the performance of a CPL detector.¹¹⁰ To investigate the relationship between chiral ligands content and optoelectronic performance of the perovskite films, we fabricated (R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films with different x values into PDs. Cr/Au electrodes were deposited on Si/SiO₂ substrates and patterned by photolithography, and then perovskite films were prepared on the substrates. We measured the photocurrents of the five devices under 447 nm illumination. Figure 4.6a and 4.6b presents the current-voltage (IV) curves of (R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films under light illumination (447 nm, 0.435 mW/cm²) and in dark. The curves exhibit the linear relationship between photocurrents and voltages, demonstrating a good Ohmic contact between perovskite films and Au electrodes. With 8 V bias, the photocurrent values of films with x = 0, 0.25, 0.5, 0.75, and 1 are 14.05 nA, 11.72 nA, 7.00 nA, 2.96 nA, and 2.32 nA, respectively. With increasing the x value from 0 to 1, the photocurrents in the films decline. This is because, with increasing the x value, the content of high-n phases tends to rise in the as-fabricated film. For quasi-2D perovskites, with n value increases, the quantum well becomes thicker, the binding energy declines and the charge carrier lifetime is thereby prolonged.^{25, 111} Therefore, with a higher content of high-n phases, the photocurrent can be improved. Another important parameter we get from Figure 4.6a and 4.6b is light on/off ratios, which is the ratio of photocurrent and dark current (Id) of the PD. With 8 V bias voltage, the light on/off ratio of films with x = 0, 0.25, 0.5, 0.75, and 1 are 0.39×10^2 (I_d = 0.36 nA), 3.26×10^2 (I_d = 0.04 nA), 2.33×10^2 (I_d = 0.03 nA), 1.1×10^2 (I_d = 0.03 nA), 1.1×10^2 (I_d = 0.02 nA), respectively. Figure 4.6c presents the responsivity (R) of PDs under 447 nm 0.486 mW/cm^2 illumination. R is given by

$$R = \frac{(I_{ph} - I_{dark})}{PS}$$
 Equation 4.2

where *P* is the light intensity, and *S* is the effective area. *R* of PDs with x = 0, 0.25, 0.5,92 0.75, and 1 are 1.57 A/W, 1.34 A/W, 1.19 A/W, 0.46 A/W, and 0.36 A/W, respectively. R declines with increasing the x value from 0 to 1, which is consistent with the trend of photocurrents. The Detectivity (D^*) of PDs is also presented in Figure 4.6b, which is given by

$$D^* = \frac{R\sqrt{S}}{\sqrt{2eI_d}}$$
 Equation 4.3

where *R* is responsivity, *S* is the effective area, *e* is the elementary charge, and I_d is the dark current. D^* is another key parameter of a PD that reflects the ability to detect light with weak intensity. As shown in Figure 4.6b, with the x value changing from 0 to 1, D^* first increases and then decreases. The PD with x = 0 presents the highest R but not the highest D^* , which can be attributed to the high I_d of the PD with x = 0.



Figure 4.6 a) I-V curves of $(R-MBA_xPEA_{1-x})_2MA_2Pb_3I_{10}$ PDs under the illumination of 0.435 mW/cm² 447 nm and b) in the dark. c) Responsivity and detectivity of $(R-MBA_xPEA_{1-x})_2MA_2Pb_3I_{10}$ films with different x values.

We further measured photocurrents of the PD fabricated with (R-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀ film under different power densities of 375 nm, 447 nm,

532 nm, 633 nm, and 750 nm lights (Figure 4.7a-e), and corresponding responsivity as a function of power density for wavelengths are shown in Figure 4.7f. (R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ PD presents broadband photo-response and the highest responsivity to 447 nm light in the tested light intensity range.



Figure 4.7 I-V curves of (R-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀ PD under different power densities of a) 375 nm, b) 447 nm, c) 532 nm, d) 633 nm and e) 750 nm lights. f) The responsivity as a function of light power density.

The noise currents of the PD fabricated with (R-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀ film were measured under 4 V bias with no illumination, as shown in Figure 4.8a, and we obtained noise spectral densities of each device by Fast Fourier Transform (FFT) from corresponding dark current noises as shown in Figure 4.8b. Dark current noises from level per unit bands (1 Hz) for (R-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀ PD is measured to be 6.8×10^{-2} pA/Hz^{1/2}. Figure 4.8c exhibits the response time of the PD of (R-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀. The rise (τ_r) and decay (τ_d) time of the device are defined as the time taken for the current increase from 10% to 90% of steady-state photocurrent and vice versa. It is shown that τ_r and τ_d are measured to be 17 ms and 34 ms, respectively.



Figure 4.8 a) Dark current noises of $(R-MBA_{0.4}PEA_{0.6})_2MA_2Pb_3I_{10}$ PD and b) the corresponding noise spectral density. c) Response speed curve of $(R-MBA_{0.4}PEA_{0.6})_2MA_2Pb_3I_{10}$ PD.

Considering both the chiroptical response and the semiconducting behavior of perovskite films, we then fabricated the CPL PD base on (R-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀

film. We measured photocurrents of (R-MBA_{0.4}PEA_{0.6})₂MA₂Pb₃I₁₀ device with 4 V bias under LCP and RCP illumination with wavelengths of 447 nm, 532 nm, and 633 nm. The CPL was generated through lasers sequentially penetrating a linear polarizer and a quarter-wave plate. As I-t curves shown in Figure 4.9b-d, the device exhibits higher photocurrents under RCP excitation than under LCP excitation. The distinguishability of CPL is always evaluated by the anisotropy factor of photocurrents (g_{Iph}), which is defined by the equation $g_{Iph} = 2(I_{RCP} - I_{LCP})/(I_{RCP} + I_{LCP})$.¹¹² I_{RCP} and I_{LCP} represent photocurrents under RCP excitation and LCP excitation, respectively. The glph under 447 nm, 532 nm, and 633 nm illumination are calculated to be 0.11, 0.19, and 0.10, respectively. The g_{Iph} is higher than the g_{CD}, which might be attributed to the chiralinduced spin selectivity and the spin-dependent carrier transition in perovskite.⁴⁹ The device is stable with repeated light on-off cycles under RCP and LCP, as shown in Figure 4.9e. We conclude that the PD is sensitive to CPL with all the three wavelengths we employed and presents g_{lph} comparable to CPL PDs based on perovskite thin films in previous works, such as S/R-MBAPbI₃ (0.1),⁵⁴ [(R)-β-MPA]₂MAPb₂ (0.2),⁵² (S- $NEA_{2}(MA)_{n-1}Pb_{n}I_{3n+1}$ (0.15),⁴⁸ and S-VPEA (0.22),¹¹³ as shown in Figure 4.9f.



Figure 4.9 a) Schematic illustration of CPL photodetection of the PD based on (R- $MBA_{0.4}PEA_{0.6})_2MA_2Pb_3I_{10}$ film. CPL measurement under b) 447, c) 532 and d) 633 nm illumination. e) I–t curves of with light on-off switch under 532 nm LCP and RCP. f) The g_{Iph} of some reported CPL PD based on perovskite thin films.

4.4 Conclusion

We fabricated a broadband circular polarized light (CPL) photodetector (PD) based on
chiral quasi-2D hybrid organic-inorganic perovskite (HOIP) thin films. First, we demonstrated that multiple quasi-2D HOIP phases can be achieved in (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ film. CD spectra of (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films exhibit wideband signals with g_{CD} of 10⁻³ level when the x value is between 0.4 and 0.8. Then, Optoelectronic performances of (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films with different x values were compared, and we fabricated the (R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films into CPL PD. The CPL detector presents wide-band photo-response to 375 nm, 447 nm, 532 nm, 633 nm, and 750 nm illuminations and presents a high responsivity of 1.07 A/W (0.742mW/cm², 447 nm). Besides, the PD exhibits CPL sensitivity in a wide wavelength region. The anisotropy factor of photocurrents (g_{1ph}) with 447 nm, 532 nm, and 633 nm CPL illumination is measured to be 0.11, 0.19, and 0.10, respectively.

Chapter 5 Controllable Regulation of Inorganic-Layer Thickness of Chiral Quasi-2D Perovskite Towards Polarization-Sensitive Photodetection

5.1 Introduction

Circular polarized light (CPL) detection has become attractive due to its application in medical science, security surveillance, and quantum computing. CPL photodetectors (PDs) are photoelectronic devices with the ability to distinguish left-handed CPL (LCP) and right-handed CPL (RCP). The performance of CPL PDs is closely related to the material's chiroptical properties and photoelectric characteristics. Organic-inorganic hybrid perovskites (HOIPs), a group of materials with high absorption coefficient⁷ and long carrier diffusion length⁶², are promising candidates for CPL PDs. Many CPL PDs based on HOIPs with chirality have been reported, such as such as (R-MBA)₂PbI₄,⁴⁴ (R-BPEA)₂PbI₄,¹⁰⁹ and (S-β-MPA)EAPbBr₄¹¹⁴.

Selection of HOIPs with suitable structures is a determining issue for the performance of HOIP-based CPL PDs. Zhu and coworkers compared photoelectric behaviors of chiral HOIPs with chained structure (1D) and layered structure (2D), and achieved selfdriven CPL PD with high photoresponse and anisotropy factor based on the 2D HOIP crystal.⁴⁹ They speculated that the high distinguishability of HOIP-CPL-PD relies on not only anisotropic absorption of CPL but also spin-dependent carrier transport and collection, in which 2D HOIPs are superior to 1D HOIPs. There are indeed many CPL PD works focused on 2D chiral HOIPs. Wu and coworkers synthesized (R-β-MPA)EAPbBr₄ crystal and fabricated ultraviolet CPL PD.¹¹⁴ Peng and coworkers realized vis-NIR dual-modal CPL PD with (R-BPEA)₂PbI₄ crystal.¹⁰⁹ Wang and coworkers fabricated CPL PD with a high anisotropic factor of 0.23 with (R)-a-(PEA)₂PbI₄ crystal.⁴⁴ Although there is much development in 2D-HOIP-based CPL PDs, charge transport is still a limitation in photoelectronic devices with 2D perovskites due to the strong quantum confinement.²⁵ Quasi-2D HOIPs have been applied in many optoelectronic fields due to their outstanding structural stability,^{76, 77} controllable phase distribution⁷⁸, and tunable bandgaps.⁷⁹ Different from 2D HOIPs with the monolayered structure, quasi-2D HOIPs possess the multilayered structure of quantum wells. In this consideration, quasi-2D HOIPs with multilayered structure are potential materials for CPL PDs with high performance.

Exploration of CPL PDs fabricated with quasi-2D HOIPs is still in the initial stages, although some impressive attempts have been made.^{52, 115} In chapter 4, we obtained HOIP films (S/R-MBA_xPEA_{1-x})₂MA₂Pb₃I₁₀ films with multiple chiral phases and thereby fabricated broadband CPL PD. In this chapter, we synthesized chiral quasi-2D HOIP crystals (S/R-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI_{3n+1} with n = 1, 2, and 3. Chiroptical and 100 photoelectric properties of crystals with different quantum well thicknesses were characterized and compared. The crystals with n = 1, 2, and 3 were fabricated into CPL PDs and achieved anisotropic factors of 0.18, 0.28, and 0.16 under 520 nm, 532 nm, and 633 nm, respectively. This work gives an insight into the components of the (S/R-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI_{3n+1} films we obtained in Chapter 4 and provides a new design strategy of chiral multilayered HOIPs in CPL detection field.

5.2 Experimental section

Materials: MAI (99.9%), PEAI (99.5%), S-MBAI (99%), R-MBAI (99%), PbI₂ (lead iodide, 99.9%), were purchased from Polymer Light Technology Corp. without further purification. Hydriodic acid (HI) solution (57 wt. %), DMF (99.8 %), and DMSO (99.9 %)were purchased from Sigma-Aldrich. Lead oxide (PbO, 99.9%) was purchased from Alfa Aesar.

Crystals Synthesis: For (S-MBA)₂PbI₄ crystal synthesis, S-MBAI and PbO powder were added into an aqueous HI/H₃PO₂ (4:1) mixture solvent with a 2:1 stoichiometric ratio. The solution was heated at 135 °C with constant magnetic stirring until the precursor powder was solved. Subsequently, the solution was cooled down to room temperature naturally. Keep the solution stationary overnight to complete crystallization. For PEA₂PbI₄ crystal synthesis, PEAI and PbO powder were added into an aqueous HI/H₃PO₂ (4:1) mixture solvent with a 2:1 stoichiometric ratio. The solution was heated at 135 °C with constant magnetic stirring until the precursor powder was solved. Subsequently, the solution was transferred into the 65 °C oven overnight to complete crystallization. For (S/R-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI_{3n+1} crystals synthesis, we added S/R-MBAI, PEAI, MAI, and PbO powders following the stoichiometric ratio of 0.8:1.2:n-1:n into aqueous HI/H₃PO₂ (4:1) mixture solvent. The solution was heated at 135 °C with constant magnetic stirring until the precursor powder was solved. Subsequently, the solution was transferred into the 65 °C oven overnight to complete crystallization. After crystallization, the crystals were removed from bottles and dried in the vacuum desiccator for 2 days.

Device Fabrication: Au electrode was patterned onto the 300-nm-thick SiO₂/p++ Si substrate by photolithography, followed by evaporation of a 35 nm thick Au layer on top of 15 nm Ti adhesion layer. The few-layer perovskites are mechanically exfoliated from bulk crystals onto a glass substrate using scotch tape. We then fabricate a transfer stamp by adhering a flat Polydimethylsiloxane (PDMS) layer to a glass slide, and then we stick Polyvinyl alcohol (PVA) on top of the PDMS. PVA film was prepared by drying 4 % PVA aqueous solution on a disk in the air for 2 days. We then adhered the transfer stamp to selected perovskites using a rotationally aligned dry transfer technique. Subsequently, we baked the stamp at 60 °C for 2 minutes to strengthen the interaction between the target material and PVA. Next, we adhered the stamp with the material 102

onto the SiO₂/Si substrate with Au electrodes.

Materials Characterization: The X-ray Diffractometer (Rigaku SmartLab 9kW) was employed to measure X-ray diffraction spectra. Absorption spectra were measured with a UV-Vis-NIR spectrometer (Perkin Elmer). Circular dichroism (CD) spectra were characterized by the CD spectrometer (JASCO J-1500 Easton, MD) at room temperature. The samples were prepared for absorption and CD measurements by grinding crystals into powder and fixed between two coverslips.

Optoelectronic Measurements: The photoresponse performance of the devices was recorded by a four-probe station (LakeShore CRX-6.5K equipped with Keithley 4200 Semiconductor Characterization System) in ambient conditions. The illumination sources were CW fiber lasers with wavelengths of 447 nm, 520 nm, 532 nm, and 633 nm. In polarized-light detection, the LEDs with 447 nm, 532 nm, and 633 nm were used as light sources. For circularly polarized light (CPL) detection, the lasers generated the CPL with 447 nm, 532 nm, and 633 nm, sequentially penetrating a linear polarizer and a quarter-wave plate.

5.3 Results

Single crystals of (R/S-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI_{3n+1} (n=1, 2, 3) were synthesized

through the temperature-decreasing process with concentrated hydroiodic acid. Phase purities of $(S-MBA_{0.4}PEA_{0.6})_2PbI_4$ (1S), $(S-MBA_{0.4}PEA_{0.6})_2PbI_4$ (1R), (S-(R-MBA_{0.4}PEA_{0.6})₂MAPb₂I₇ MBA_{0.4}PEA_{0.6})₂MAPb₂I₇ (2S), (2R), (S- $MBA_{0.4}PEA_{0.6})_2MA_2Pb_3I_{10}$ (3S), and $(R-MBA_{0.4}PEA_{0.6})_2MA_2Pb_3I_{10}$ (3R) were confirmed by the single crystal XRD (Figure 5.1). The XRD patterns of (S-MBA)₂PbI₄ and PEA₂PbI₄ were also presented in Figure 5.1 for comparison. For 1R and 1S, the diffraction peaks start from 5.42° corresponding to (002) planes. The location of 1R/1S (002) diffraction peaks is different from that of S-MBA₂PbI₄ crystals but is close to the location of (002) diffraction peaks of PEA₂PbI₄,¹¹⁶ which indicates the inter-planer spacing of 1R and 1S is mainly depended on PEA⁺ ligands rather than S/R-MBA⁺ ligands. For 2R, 2S, 3R, and 3S, the 2 theta values of diffraction peaks reduce with the perovskite quantum well thickness increasing from 2 to 3. For example, the (080) diffraction peaks of 2R/2S and 3R/3S are located at 15.9° and 12.0°, respectively. The repetition of (0k0) group suggests quasi-2D perovskites with n > 1 tend to orient along [101] direction.¹¹⁷



Figure 5.1 XRD patterns of $(S/R-MBA_{0.4}PEA_{0.6})_2MA_{n-1}Pb_nI_{3n+1}$ crystals with $n = 1, 2, 3, and (S-MBA)_2PbI_4$.

Ultraviolet-visible spectra and circular dichroism (CD) spectra were performed to characterize the optical properties of the single crystals (Figure 5.2). The crystals were prepared into powder for the measurement. All the crystals show sharp excitonic absorption resonances, and the band gap energy declines with the n value increasing from 1 to 3, which can be attributed to the weakened quantum confinement.¹¹⁸ For all 3 pairs of crystals, R and S samples present opposite CD signals near the excitonic absorption resonances, different from those of the S/R-MBA located at the ultraviolet ¹⁰⁵

region.⁵⁴ The CD spectra of crystals indicate that the chirality of ligands has been transferred into the perovskite framework, so CD signals appear at the excitonic absorption band of perovskites.



Figure 5.2 Absorbance spectra, CD spectra of $(S/R-MBA_xPEA_{1-x})_2MA_2Pb_3I_{10}$ crystals with a) n = 1, b) n = 2, and c) n = 3.

To further demonstrate the chiral ligands embedded into the perovskite crystals, we prepared thin films by solving the 1S/R, 2S/R, and 3S/R in DMF and spin-coating with as obtained solutions. Figure 5.3 shows the absorption spectra and CD spectra of the films. The absorption spectra of films obtained from crystals 1S and 1R exhibit a sharp peak at 507 nm (Figure 5.3a), and the CD spectra of 1S and 1R films present opposite signals at 504 nm and 514 nm (Figure 5.3d). For films obtained from 2S and 2R crystals, the absorption spectra exhibit peaks at 563 nm (Figure 5.3b), and the opposite CD signals occur at 527 nm and 565 nm (Figure 5.3e). The absorption and CD spectra of films obtained from 3S and 3R crystals exhibit multiple peaks (Figure 5.3c, 5.3f), which

can be attributed to multiple phases formed in the spin-coating process. The absorption peaks are located at 507 nm, 563 nm, and 611 nm, and peaks in CD spectra at 512 nm, 564 nm, and 614 nm. The obvious CD signals in films obtained from 1S/R, 2S/R, and 3S/R crystals prove that the chiral ligands S-MBA and R-MBA participate in the growth of the crystals.



Figure 5.3 Absorbance spectra, CD spectra of $(S/R-MBA_xPEA_{1-x})_2MA_2Pb_3I_{10}$ crystals with a) n=1, b) n = 2, and c) n = 3.

To investigate the photoelectric characteristics of the chiral perovskite crystals, we fabricated photodetectors based on single crystals 1R, 2R, and 3R (abbreviated as 1R-PD, 2R-PD, and 3R-PD, respectively) along the (001) plane. As shown in Figure 5.4a, we patterned Ti/Au electrodes on the Si/SiO₂ substrates and then transferred perovskite layers (exfoliated from bulk crystals) onto the electrodes. Figure 5.4b presents I-V curves of 1R-PD, 2R-PD, and 3R-PD in dark and under 447 nm illumination. The I-t 107

curves present the linear relationship between photocurrents and voltages, demonstrating a good Ohmic contact between crystals and Au electrodes. Under 4 V bias, the dark current (Idark) of 1R-PD is below 1.5 pA, and Idark of 2R-PD and 3R-PD are below 2 pA. The low Idark values indicate high crystal qualities of 1R-PD, 2R-PD, and 3R-PD. With 0.743 mW/cm² 447 nm illumination, the photocurrent under 4 V bias of 1R-PD is 45.0 pA, and the on-off ratio is calculated to be 30. Under the same condition, the photocurrents of 2R-PD and 3R-PD reach 0.88 nA and 1.04 nA, and the corresponding on-off ratios are 440 and 578, respectively. The photocurrents and on/off ratio of 2R-PD and 3R-PD are an order of magnitude higher than 1R-PD. With increasing the n value from 1 to 3, the photocurrents and on-off ratios of PDs based on $(R-MBA_{0,4}PEA_{0,6})_2MA_{n-1}Pb_nI_{3n+1}$ crystals rise. This is because the binding energy declines for quasi-2D perovskites with thicker quantum wells, and the charge carrier lifetime is thereby prolonged. Figure 5.4c exhibits the I-t curves of 1R-PD, 2R-PD, and 3R-PD with a light on-off switch (447 nm, 0.743 mW/cm²). It can be proven that 1R-PD, 2R-PD, and 3R-PD are stable with repeated light on-off cycles. Figures 5.4d, 5.4e, and 5.4f present I-V curves of 1R-PD, 2R-PD, and 3R-PD under illumination (447 nm) with power density increasing from 0.435 to 5.811 mW/cm². With the light power density rising, photocurrents of three PDs increase. Under the same illumination power density, the photocurrents of 1R-PD, 2R-PD, and 3R-PD sequentially increase.



Figure 5.4 a) Schematic illustration of the PD fabricated with perovskite crystals. b) I-V curves of 1R-PD, 2R-PD, and 3R-PD under 447 nm 0.743 mW/cm². c) I-t curves of 1R-PD, 2R-PD, and 3R-PD with repeated light on-off cycles. I-V curves of d) 1R-PD, e) 2R-PD, and f) 3R-PD under different power densities of 447 nm illumination.

Figure 5.5 presents the response time of 1R-PD, 2R-PD, and 3R-PD under 447 nm illumination. The rise (τ_r) and decay (τ_d) time of the device are defined as the time taken for the current increase from 10% to 90% of steady-state photocurrent and vice versa. I-t curves in Figures 5.5a, 5.5b, and 5.5c prove that τ_r and τ_d of 1R-PD, 2R-PD, and 3R-PD are shorter than the minimum time interval (34 ms).



Figure 5.5 Response speed curve of a) 1R-PD, b) 2R-PD, and c) 3R-PD.

The noise currents of 1R-PD, 2R-PD, and 3R-PD were measured under a 4 V bias in the dark, as shown in Figures 5.6a, 5.6c, and 5.6e, respectively. We obtained noise spectral densities of each PD via Fast Fourier Transform (FFT) from the dark current noises.^{76, 88} Figures 5.6b, 5.6d, and 5.6f show noise spectral densities calculated from 5.6a, 5.6c, and 5.6e, and current noises from level per unit bands (1 Hz) for 1R-PD, 2R-PD, and 3R-PD are measured to be 0.11, 0.45, and 0.38 pA/Hz^{1/2}, respectively.



Figure 5.6 Dark current noises of a) 1R-PD, c) 2R-PD, and e) 3R-PD, and corresponding noise spectral densities of b) 1R-PD, d) 2R-PD, and f) 3R-PD.

We further measured the CPL detection capabilities of 1R-PD, 2R-PD, and 3R-PD. Referring to the CD spectra of 1R, 2R, and 3R crystals, we select illuminations with wavelengths of 520 nm, 532 nm, and 633 nm to perform the 1R-PD, 2R-PD, and 3R-PD measurements. The CPL was generated through lasers sequentially penetrating a linear polarizer and a quarter-wave plate, as shown in Figure 5.7a. Photocurrents with 4 V bias under LCP and RCP illumination (abbreviated as I_{LCP} and I_{RCP}, respectively) of 1R-PD, 2R-PD, and 3R-PD are presented as I-t curves in Figure 5.7b, 5.7c, and 5.7d, respectively. 1R-PD, 2R-PD, and 3R-PD all presented higher I_{RCP} than I_{LCP}. The distinguishability of CPL is always evaluated by the anisotropy factor of photocurrents (g_{1ph}), which is defined by the equation $g_{1ph} = 2(I_{RCP} - I_{LCP})(I_{RCP} + I_{LCP})$.¹¹² The g_{1ph} for 1R-PD, 2R-PD, and 3R-PD under 420 nm, 532 nm, and 633 nm illumination are calculated to be 0.18, 0.28, and 0.16, respectively. This series of PDs fabricated with (R-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI_{3n+1} (n=1, 2, 3) crystals show the ability to detect CPL with different wavelengths, and present high g_{1ph} among CPL PD based on chiral perovskite crystal, such as (R-MBA)₂PbI₄ (0.23),⁴⁴ (R-BPEA)₂PbI₄ (0.13),¹⁰⁹ (S-β-MPA)EAPbBr₄ (0.19),¹¹⁴ [(R)-β-MPA]₂MAPb₂I₇ (0.11),⁵² etc. (Figure 5.7d).



Figure 5.7 a) Schematic illustration of CPL photodetection of the PD based on chiral 112

crystals. CPL measurement of b) 1R-PD, c) 2R-PD, and d) 3R-PD. f) The g_{Iph} of some reported CPL PD based on chiral perovskite crystals.

5.4 Conclusion

We obtained chiral HOIP crystals (S/R-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI_{3n+1} with n = 1, 2, and 3. Optical characterizations show that as the quantum well width (n value) increases, the band gap energy of the crystals decreases, and a circular dichroism signal appears near the excitonic absorption resonance, indicating the differential absorption of LCP and RCP. The optoelectronic measurements demonstrated that photoelectric characteristics improve from n = 1 to n = 3, which is attributed to the weakening of quantum confinement effects. The crystals with n = 1, 2, and 3 were fabricated into CPL PDs and achieved anisotropic factors of 0.18, 0.28, and 0.16 under 520 nm, 532 nm, and 633 nm, respectively.

Chapter 6 Conclusions and Future Work 6.1 Conclusions

In this thesis, we reviewed the applications, mechanisms, and parameters of photodetectors, and we focused on summarizing polarized photodetectors based on organic-inorganic hybrid perovskites (HOIPs). We noticed some challenging issues so far: i) HOIP photodetectors for linearly polarized light (LPL) require higher optoelectronic performances and more feasible fabrication methods; ii) Chiral 2D HOIPs are a group of promising materials of circularly polarized light (CPL) photodetectors. However, they feature wide bandgaps, which limit the CPL detection region and suppress the optoelectronic performance of the device. iii) Quasi-2D HOIPs with chirality are a potential candidate for (CPL) photodetectors, but their exploration is still in the initial stages. This thesis contains three works exploring solutions to the barriers above.

First, we fabricated an LPL photodetector based on a quasi-2D HOIP thin film. The device achieved a polarization sensitivity of 1.68, responsivity of 89.8 A/W, and detectivity of 1.5×10^{12} Jones. The function of polarization detection arises from the nanoimprinted linear pattern on the film's surface. Besides, the linear pattern also enhances light harvest, improving the photodetector performance. The spatial separation of low-dimensional phases and 3D-like phases resulting from hot-casting

was demonstrated by transient absorption (TA) and photoluminescence spectra. The charge carrier dynamics studied from TA spectra reveal the efficient charge funneling from small-n phases gathered at the bottom of the film to the top high-n phases, forming a photogating structure. The behavior of the charge carriers contributes to an extended carrier lifetime, which enhances the photodetector's responsivity. Our experiments have validated the feasibility of fabricating polarization-sensitive PD on quasi-2D HOIP thin films. This research is expected to advance the development of high-performance polarization-sensitive photodetectors.

Second, we developed a broadband CPL PD with chiral quasi-2D HOIP thin films. Initially, we found the circular dichroism (CD) spectra of hot-casted (S/R-MBA_xPEA₁. x)₂MA₂Pb₃I₁₀ films show wide-band signals with a g_{CD} level of 10⁻³ when the x value ranges from 0.4 to 0.8, which proves multiple quasi-2D phases exist in the films. Subsequently, we compared the optoelectronic performances of (S/R-MBA_xPEA₁. x)₂MA₂Pb₃I₁₀ films with varying x values. Then, we fabricated (R-MBA_xPEA₁. x)₂MA₂Pb₃I₁₀ films into CPL photodetectors. The CPL detector exhibits a broad photoresponse to illuminations at 375 nm, 447 nm, 532 nm, 633 nm, and 750 nm, achieving a high responsivity of 1.07 A/W at 447 nm (0.742 mW/cm²). Additionally, the photodetector demonstrates CPL sensitivity under 447 nm, 532 nm, and 633 nm illumination and reaches an anisotropy factor of photocurrents (g_{Iph}) of 0.11, 0.19, and 0.10, respectively. Third, we synthesized chiral HOIP crystals (S/R-MBA_{0.4}PEA_{0.6})₂MA_{n-1}Pb_nI_{3n+1} with n = 1, 2, and 3. Optical characterizations revealed that as the n value increases, the band gap energy of the crystals decreases. A circular dichroism signal also emerges near the excitonic absorption resonance, indicating differential absorption of left- and right-circularly polarized light. Optoelectronic measurements showed that the photoelectric characteristics improved from n = 1 to n = 3, attributed to the reduction in quantum confinement effects. The crystals with n = 1, 2, and 3 were fabricated into CPL photodetectors, achieving anisotropic factors of 0.18, 0.28, and 0.16 at 520 nm, 532 nm, and 633 nm, respectively.

6.2 Future work

Quasi-2D chiral HOIPs are a promising material for CPL photodetectors. We investigated the chiroptical and photoelectric properties of $(S/R-MBA_{0.4}PEA_{0.6})2MA_{n-1}PbnI_{3n+1}$, and fabricated CPL photodetectors with the crystals. However, several works are still in progress or worth attempting in the future.

First, analyze the crystal structures of $(S/R-MBA_{0.4}PEA_{0.6})_2MA_{n-1}Pb_nI_{3n+1}$ with n = 1, 2, 3, and attempt to fabricate self-powered CPL-sensitive photodetectors with the crystals. We shall employ single-crystal X-ray measurement to characterize the crystals and solve the structure of the crystals. With a deep understanding of the crystal structure, we can construct self-driven photodetectors relying on the polar photovoltaic effect of HOIP crystals.⁴⁹

Second, spin dynamics study of chiral quasi-2D HOIPs. Long spin lifetime is favorable in spintronics applications. With circularly polarized transient absorption measurement, we can investigate the spin relaxation process of chiral quasi-2D HOIP thin films. By comparing the spin lifetime of chiral quasi-2D HOIP thin films and chiral 2D HOIP thin films, we can study the impacts of quantum well width on spin lifetime in chiral HOIP.

References

 Ndagano, B.; Perez-Garcia, B.; Roux, F. S.; McLaren, M.; Rosales-Guzman, C.; Zhang, Y.; Mouane, O.; Hernandez-Aranda, R. I.; Konrad, T.;
 Forbes, A., Characterizing quantum channels with non-separable states of classical light. *Nat Phys* 2017, *13* (4), 397-402.

He, C.; He, H.; Chang, J.; Chen, B.; Ma, H.; Booth, M. J., Polarisation optics for biomedical and clinical applications: a review. *Light Sci Appl* 2021, *10* (1), 194.

3. Tuniyazi, A.; Mu, T.; Jiang, X.; Han, F.; Li, H.; Li, Q.; Gong, H.; Wang, W.; Qin, B., Snapshot polarized light scattering spectroscopy using spectrally-modulated polarimetry for early gastric cancer detection. *J Biophotonics* **2021**, *14* (9), e202100140.

Qiu, L.; Pleskow, D. K.; Chuttani, R.; Vitkin, E.; Leyden, J.; Ozden, N.;
 Itani, S.; Guo, L.; Sacks, A.; Goldsmith, J. D.; Modell, M. D.; Hanlon, E. B.;
 Itzkan, I.; Perelman, L. T., Multispectral scanning during endoscopy guides biopsy of dysplasia in Barrett's esophagus. *Nat Med* 2010, *16* (5), 603-6, 1p following 606.

5. Wang, Z.; Peng, Y.; Shi, C.; Wang, L.; Chen, X.; Wu, W.; Wu, X.; Zhu, Y.; Zhang, J.; Cheng, G.; Zhuang, S., Qualitative and quantitative recognition of chiral drugs based on terahertz spectroscopy. *Analyst* **2021**, *146* (12), 3888-3898.

 Hou, H. Y.; Tian, S.; Ge, H. R.; Chen, J. D.; Li, Y. Q.; Tang, J. X., Recent Progress of Polarization - Sensitive Perovskite Photodetectors. *Adv Funct Mater* 2022, 118 32 (48), 2209324.

 Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. I., Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells. *Nat. Mater.* 2014, *13* (9), 897-903.

 Xing, G., Nripan M., Shuangyong S., Swee S. L., Yeng M. L., Michael G., Subodh M., Tze C. S., Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH3NH3PbI3. *science* 2013, *342* (6165).

9. Yamamoto, H.; Carreira, E. M., Comprehensive chirality. Newnes: 2012; Vol. 1.

10. Sang, Y.; Han, J.; Zhao, T.; Duan, P.; Liu, M., Circularly Polarized Luminescence in Nanoassemblies: Generation, Amplification, and Application. *Adv Mater* **2020**, *32* (41), e1900110.

Sweeney, A.; Jiggins, C.; Johnsen, S., Polarized light as a butterfly mating signal.
 Nature 2003, *423* (6935), 31-32.

 Gagnon, Yakir L.; Templin, Rachel M.; How, Martin J.; Marshall, N. J., Circularly Polarized Light as a Communication Signal in Mantis Shrimps. *Current Biology* 2015, 25 (23), 3074-3078.

13. Tyo, J. S.; Goldstein, D. L.; Chenault, D. B.; Shaw, J. A., Review of passive imaging polarimetry for remote sensing applications. *Appl. Opt.* **2006**, *45* (22), 5453-5469.

14. Wu, D.; Zhang, Y.; Liu, C.; Sun, Z.; Wang, Z.; Lin, Z.; Qiu, M.; Fu,
D.; Wang, K., Recent Progress of Narrowband Perovskite Photodetectors: Fundamental 119

Physics and Strategies. Advanced Devices & Instrumentation 2023, 4.

15. Fang, H.; Hu, W., Photogating in Low Dimensional Photodetectors. *Adv Sci* 2017, 4 (12), 1700323.

16. Lu, X.; Sun, L.; Jiang, P.; Bao, X., Progress of Photodetectors Based on the Photothermoelectric Effect. *Adv Mater* **2019**, *31* (50), e1902044.

17. KEI, H.; RYOSUKE, S.; JOHN, H., Perovskite in Earth's deep interior. *science*2017, *358* (6364): 734-738.

 Wu, H. S.; Murti, B. T.; Singh, J.; Yang, P. K.; Tsai, M. L., Prospects of Metal-Free Perovskites for Piezoelectric Applications. *Adv Sci* 2022, *9* (12), e2104703.
 Lian, Z.; Yan, Q.; Lv, Q.; Wang, Y.; Liu, L.; Zhang, L.; Pan, S.; Li, Q.; Wang, L.; Sun, J. L., High-Performance Planar-Type Photodetector on (100) Facet of MAPbI3 Single Crystal. *Sci Rep* 2015, *5*, 16563.

20. Soe, C. M. M.; Stoumpos, C. C.; Kepenekian, M.; Traore, B.; Tsai, H.; Nie, W.; Wang, B.; Katan, C.; Seshadri, R.; Mohite, A. D.; Even, J.; Marks, T. J.; Kanatzidis, M. G., New Type of 2D Perovskites with Alternating Cations in the Interlayer Space, (C(NH(2))(3))(CH(3)NH(3))(n)Pb(n)I(3n+1): Structure, Properties, and Photovoltaic Performance. *J Am Chem Soc* **2017**, *139* (45), 16297-16309.

21. Yu, S.; Liu, P.; Xiao, S., A review of main characterization methods for identifying two-dimensional organic–inorganic halide perovskites. *J Mater Sci* 2021, *56* (20), 11656-11681.

22. Chen, Y.; Sun, Y.; Peng, J.; Tang, J.; Zheng, K.; Liang, Z., 2D Ruddlesden-120 Popper Perovskites for Optoelectronics. Adv Mater 2018, 30 (2), 1703487.

23. Mao, L.; Ke, W.; Pedesseau, L.; Wu, Y.; Katan, C.; Even, J.;
Wasielewski, M. R.; Stoumpos, C. C.; Kanatzidis, M. G., Hybrid Dion-Jacobson 2D
Lead Iodide Perovskites. *J Am Chem Soc* 2018, *140* (10), 3775-3783.

24. Fu, P.; Liu, Y.; Yu, S.; Yin, H.; Yang, B.; Ahmad, S.; Guo, X.; Li, C., Dion-Jacobson and Ruddlesden-Popper double-phase 2D perovskites for solar cells. *Nano Energy* **2021**, *88*, 106249.

25. Blancon, J. C.; Stier, A. V.; Tsai, H.; Nie, W.; Stoumpos, C. C.; Traore, B.;
Pedesseau, L.; Kepenekian, M.; Katsutani, F.; Noe, G. T.; Kono, J.; Tretiak,
S.; Crooker, S. A.; Katan, C.; Kanatzidis, M. G.; Crochet, J. J.; Even, J.;
Mohite, A. D., Scaling law for excitons in 2D perovskite quantum wells. *Nat Commun*2018, 9 (1), 2254.

26. Fang, C.; Xu, M.; Ma, J.; Wang, J.; Jin, L.; Xu, M.; Li, D., Large Optical Anisotropy in Two-Dimensional Perovskite [CH(NH2)2][C(NH2)3]PbI4 with Corrugated Inorganic Layers. *Nano Lett* **2020**, *20* (4), 2339-2347.

27. Zhang, W.; Hong, M.; Luo, J., Centimeter-Sized Single Crystal of a One-Dimensional Lead-Free Mixed-Cation Perovskite Ferroelectric for Highly Polarization Sensitive Photodetection. *J Am Chem Soc* **2021**, *143* (40), 16758-16767.

28. Zeng, L. H.; Chen, Q. M.; Zhang, Z. X.; Wu, D.; Yuan, H.; Li, Y. Y.; Qarony, W.; Lau, S. P.; Luo, L. B.; Tsang, Y. H., Multilayered PdSe2/Perovskite Schottky Junction for Fast, Self - Powered, Polarization - Sensitive, Broadband 121 Photodetectors, and Image Sensor Application. Adv Sci 2019, 6 (19).

29. Feng, J.; Yan, X.; Liu, Y.; Gao, H.; Wu, Y.; Su, B.; Jiang, L., Crystallographically Aligned Perovskite Structures for High-Performance Polarization-Sensitive Photodetectors. *Adv Mater* **2017**, *29* (16), 1605993.

30. Pan, S.; Zou, H.; Wang, A. C.; Wang, Z.; Yu, J.; Lan, C.; Liu, Q.;
Wang, Z. L.; Lian, T.; Peng, J.; Lin, Z., Rapid Capillary-Assisted Solution Printing of Perovskite Nanowire Arrays Enables Scalable Production of Photodetectors. *Angew Chem Int Ed Engl* 2020, *59* (35), 14942-14949.

31. Li, S.-X.; Zhang, G.-P.; Xia, H.; Xu, Y.-S.; Lv, C.; Sun, H.-B., Templateconfined growth of Ruddlesden–Popper perovskite micro-wire arrays for stable polarized photodetectors. *Nanoscale* **2019**, *11* (39), 18272-18281.

32. Jeong, B.; Han, H.; Kim, H. H.; Choi, W. K.; Park, Y. J.; Park, C., Polymer-Assisted Nanoimprinting for Environment- and Phase-Stable Perovskite Nanopatterns. *ACS Nano* **2020**, *14* (2), 1645-1655.

33. Gao, L.; Zeng, K.; Guo, J.; Ge, C.; Du, J.; Zhao, Y.; Chen, C.; Deng,
H.; He, Y.; Song, H.; Niu, G.; Tang, J., Passivated Single-Crystalline
CH(3)NH(3)PbI(3) Nanowire Photodetector with High Detectivity and Polarization
Sensitivity. *Nano Lett* 2016, *16* (12), 7446-7454.

34. Zhou, Y.; Luo, J.; Zhao, Y.; Ge, C.; Wang, C.; Gao, L.; Zhang, C.; Hu,
M.; Niu, G.; Tang, J., Flexible Linearly Polarized Photodetectors Based on All Inorganic Perovskite CsPbI3 Nanowires. *Adv Opt Mater* 2018, 6 (22), 1800679.

35. Wang, H.; Haroldson, R.; Balachandran, B.; Zakhidov, A.; Sohal, S.;
Chan, J. Y.; Zakhidov, A.; Hu, W., Nanoimprinted Perovskite Nanograting
Photodetector with Improved Efficiency. ACS Nano 2016, 10 (12), 10921-10928.

36. Wang, M.; Tian, W.; Cao, F.; Wang, M.; Li, L., Flexible and Self - Powered Lateral Photodetector Based on Inorganic Perovskite CsPbI3–CsPbBr3 Heterojunction Nanowire Array. *Adv. Funct. Mater.* **2020**, *30* (16), 1909771.

37. Zhan, Y.; Wang, Y.; Cheng, Q.; Li, C.; Li, K.; Li, H.; Peng, J.; Lu, B.;
Wang, Y.; Song, Y.; Jiang, L.; Li, M., A Butterfly-Inspired Hierarchical Light-Trapping Structure towards a High-Performance Polarization-Sensitive Perovskite
Photodetector. *Angew Chem Int Ed Engl* 2019, *58* (46), 16456-16462.

Song, Q.; Wang, Y.; Vogelbacher, F.; Zhan, Y.; Zhu, D.; Lan, Y.; Fang,
 W.; Zhang, Z.; Jiang, L.; Song, Y.; Li, M., Moir é Perovskite Photodetector
 toward High - Sensitive Digital Polarization Imaging. *Adv Energy Mater* 2021, *11* (29).
 Zhang, J.; Guo, Q.; Li, X.; Li, C.; Wu, K.; Abrahams, I.; Yan, H.;
 Knight, M. M.; Humphreys, C. J.; Su, L., Solution-Processed Epitaxial Growth of
 Arbitrary Surface Nanopatterns on Hybrid Perovskite Monocrystalline Thin Films. *ACS Nano* 2020, *14* (9), 11029-11039.

40. Zhang, J.; Zhao, J.; Zhou, Y.; Wang, Y.; Blankenagel, K. S.; Wang, X.;
Tabassum, M.; Su, L., Polarization - Sensitive Photodetector Using Patterned
Perovskite Single - Crystalline Thin Films. *Adv Opti Mater* 2021, *9* (17), 2100524.

41. Ye, H.-Y.; Tang, Y.-Y.; Li, P.-F.; Liao, W.-Q.; Gao, J.-X.; Hua, X.-N.; 123 Cai, H.; Shi, P.-P.; You, Y.-M.; Xiong, R.-G. J. S., Metal-free three-dimensional perovskite ferroelectrics. *science* **2018**, *361* (6398), 151-155.

42. Long, G.; Zhou, Y.; Zhang, M.; Sabatini, R.; Rasmita, A.; Huang, L.; Lakhwani, G.; Gao, W. J. A. M., Theoretical prediction of chiral 3D hybrid organic–inorganic perovskites. *Adv Mater* **2019**, *31* (17), 1807628.

43. Chen, G.; Liu, X.; An, J.; Wang, S.; Zhao, X.; Gu, Z.; Yuan, C.; Xu, X.; Bao, J.; Hu, H.-S.; Li, J.; Wang, X., Nucleation-mediated growth of chiral 3D organic–inorganic perovskite single crystals. *Nat Chem* **2023**, *15* (11), 1581-1590.

44. Wang, J.; Fang, C.; Ma, J.; Wang, S.; Jin, L.; Li, W.; Li, D., Aqueous Synthesis of Low-Dimensional Lead Halide Perovskites for Room-Temperature Circularly Polarized Light Emission and Detection. *ACS Nano* 2019, *13* (8), 9473-9481.
45. LU, H.; WANG, J.; CHUANXIAO XIAO; XIN PAN; CHEN, X.; ROMAN BRUNECKY; BERRY, J. J.; ZHU, K.; BEARD, M. C.; VARDENY, Z. V., Spin-dependent charge transport through 2D chiral hybrid lead-iodide perovskites. *Sci Adv* 2019, *5* (12), eaay0571.

46. Ma, J.; Fang, C.; Chen, C.; Jin, L.; Wang, J.; Wang, S.; Tang, J.; Li, D.,
Chiral 2D Perovskites with a High Degree of Circularly Polarized Photoluminescence.
ACS Nano 2019, 13 (3), 3659-3665.

47. Ishii, A.; Miyasaka1, T., Direct detection of circular polarized light in helical 1D perovskite-based photodiode. *Sci Adv* **2020**, *6* (46), eabd3274.

48. Liu, T.; Shi, W.; Tang, W.; Liu, Z.; Schroeder, B. C.; Fenwick, O.; Fuchter, 124

M. J., High Responsivity Circular Polarized Light Detectors based on Quasi Two-Dimensional Chiral Perovskite Films. *ACS Nano* **2022**, *16* (2), 2682-2689.

49. Zhu, T.; Weng, W.; Ji, C.; Zhang, X.; Ye, H.; Yao, Y.; Li, X.; Li, J.;
Lin, W.; Luo, J., Chain-to-Layer Dimensionality Engineering of Chiral Hybrid
Perovskites to Realize Passive Highly Circular-Polarization-Sensitive Photodetection.
J Am Chem Soc 2022, 144 (39), 18062-18068.

50. Zhu, Z. K.; Zhu, T.; You, S.; Yu, P.; Wu, J.; Zeng, Y.; Jiang, Y.; Liu, X.; Li, L.; Ji, C.; Luo, J., Regulating Circularly Polarized Light Detection via Polar-Phase Transition in Alternating Chiral-Achiral Cations Intercalation-Type Hybrid Perovskites. *Adv Sci* **2024**, *11* (6), e2307593.

51. Huang, P.-J.; Taniguchi, K.; Miyasaka, H., Bulk Photovoltaic Effect in a Pair of Chiral–Polar Layered Perovskite-Type Lead Iodides Altered by Chirality of Organic Cations. *J Am Chem Soc* **2019**, *141* (37), 14520-14523.

52. Wang, L.; Xue, Y.; Cui, M.; Huang, Y.; Xu, H.; Qin, C.; Yang, J.; Dai,
H.; Yuan, M., A Chiral Reduced-Dimension Perovskite for an Efficient Flexible
Circularly Polarized Light Photodetector. *Angew Chem Int Ed Engl* 2020, *59* (16),
6442-6450.

53. Billing, D. G.; Lemmerer, A., Bis[(S)-[beta]-phenethylammonium] tribromoplumbate(II). *Acta Crystallographica Section E* **2003**, *59* (6), m381-m383.

54. Chen, C.; Gao, L.; Gao, W.; Ge, C.; Du, X.; Li, Z.; Yang, Y.; Niu, G.;
 Tang, J., Circularly polarized light detection using chiral hybrid perovskite. *Nat* 125

Commun **2019**, *10* (1), 1927.

55. Xu, L.; Wang, X.; Wang, W.; Sun, M.; Choi, W. J.; Kim, J. Y.; Hao, C.;
Li, S.; Qu, A.; Lu, M.; Wu, X.; Colombari, F. M.; Gomes, W. R.; Blanco, A.
L.; de Moura, A. F.; Guo, X.; Kuang, H.; Kotov, N. A.; Xu, C., Enantiomerdependent immunological response to chiral nanoparticles. *Nature* 2022, 601 (7893), 366-373.

56. He, C.; Qiu, J.; Mu, Z.; Chen, J.; Wu, Y.; Jiang, Z.; Zhang, P.; Qin, X.; Xing, G.; Liu, X., Room temperature circularly polarized emission in perovskite nanocrystals through bichiral-molecule-induced lattice reconstruction. *Matter* **2024**, *7* (2), 475-484.

57. Yu, Z. G., Chirality-Induced Spin-Orbit Coupling, Spin Transport, and Natural Optical Activity in Hybrid Organic-Inorganic Perovskites. *J Phys Chem Lett* 2020, *11* (20), 8638-8646.

58. Lu, H., Wang, J., Xiao, C., Pan, X., Chen, X., Brunecky, R., Berry, J.J., Zhu, K., Beard, M.C. and Vardeny, Z.V., Spin-dependent charge transport through 2D chiral hybrid lead-iodide perovskites. *Sci adv* **2019**, 5(12), 0571.

59. Smith, D. S.; Eremin, S. A., Fluorescence polarization immunoassays and related methods for simple, high-throughput screening of small molecules. *Anal. Bioanal. Chem.* **2008**, *391* (5), 1499-507.

60. Breckinridge, J.; Oppenheimer, B., Polarization Effects in Reflecting
 Coronagraphs for White Light Applications in Astronomy. *Astrophys. J. Lett.* 2003, 600.

61. Yin, K.; Zhan, T.; Xiong, J.; He, Z.; Wu, S.-T., Polarization Volume Gratings for Near-Eye Displays and Novel Photonic Devices. *Crystals* **2020**, *10* (7), 561.

62. Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C., Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH3NH3PbI3. *Science* **2013**, *342* (6156), 344-347.

63. Chen, Y.; Yin, J.; Wei, Q.; Wang, C.; Wang, X.; Ren, H.; Yu, S. F.; Bakr, O. M.; Mohammed, O. F.; Li, M., Multiple exciton generation in tin–lead halide perovskite nanocrystals for photocurrent quantum efficiency enhancement. *Nat. Photonics* **2022**, *16* (7), 485-490.

64. Zhuang, L.; Wei, Q.; Li, C.; Ren, H.; Li, Y.; Shi, F.; Zhai, L.; Leng, K.;
Li, M.; Lau, S. P., Efficient Light - Emitting Diodes via Hydrogen Bonding Induced
Phase Modulation in Quasi - 2D Perovskites. *Adv. Opt. Mater.* 2022, *10* (21), 2201180.
65. Yang, T.; Li, Y.; Han, S.; Xu, Z.; Liu, Y.; Zhang, X.; Liu, X.; Teng, B.;
Luo, J.; Sun, Z., Highly-Anisotropic Dion-Jacobson Hybrid Perovskite by Tailoring
Diamine into CsPbBr(3) for Polarization-Sensitive Photodetection. *Small* 2020, *16* (14), e1907020.

66. Fang, C.; Xu, M.; Ma, J.; Wang, J.; Jin, L.; Xu, M.; Li, D., Large Optical Anisotropy in Two-Dimensional Perovskite [CH(NH(2))(2)][C(NH(2))(3)]PbI(4) with Corrugated Inorganic Layers. *Nano Lett.* **2020**, *20* (4), 2339-2347.

67. Zeng, L. H.; Chen, Q. M.; Zhang, Z. X.; Wu, D.; Yuan, H.; Li, Y. Y.; Qarony, W.; Lau, S. P.; Luo, L. B.; Tsang, Y. H., Multilayered PdSe(2)/Perovskite Schottky Junction for Fast, Self-Powered, Polarization-Sensitive, Broadband Photodetectors, and Image Sensor Application. *Adv. Sci.* **2019**, *6* (19), 1901134.

68. Lu, L.; Weng, W.; Ma, Y.; Liu, Y.; Han, S.; Liu, X.; Xu, H.; Lin, W.; Sun, Z.; Luo, J., Anisotropy in a 2D Perovskite Ferroelectric Drives Self-Powered Polarization-Sensitive Photoresponse for Ultraviolet Solar-Blind Polarized-Light Detection. *Angew. Chem., Int. Ed.* **2022**, *61* (26), e202205030.

69. Feng, J.; Yan, X.; Liu, Y.; Gao, H.; Wu, Y.; Su, B.; Jiang, L., Crystallographically Aligned Perovskite Structures for High-Performance Polarization-Sensitive Photodetectors. *Adv. Mater.* **2017**, *29* (16).

70. Pan, S.; Zou, H.; Wang, A. C.; Wang, Z.; Yu, J.; Lan, C.; Liu, Q.;
Wang, Z. L.; Lian, T.; Peng, J.; Lin, Z., Rapid Capillary-Assisted Solution Printing of Perovskite Nanowire Arrays Enables Scalable Production of Photodetectors. *Angew. Chem., Int. Ed.* 2020, *59* (35), 14942-14949.

71. Gao, L.; Zeng, K.; Guo, J.; Ge, C.; Du, J.; Zhao, Y.; Chen, C.; Deng,
H.; He, Y.; Song, H.; Niu, G.; Tang, J., Passivated Single-Crystalline
CH3NH3PbI3 Nanowire Photodetector with High Detectivity and Polarization
Sensitivity. *Nano Lett.* 2016, *16* (12), 7446-7454.

72. Zhou, Y.; Luo, J.; Zhao, Y.; Ge, C.; Wang, C.; Gao, L.; Zhang, C.; Hu,
M.; Niu, G.; Tang, J., Flexible Linearly Polarized Photodetectors Based on All-Inorganic Perovskite CsPbI3 Nanowires. *Adv. Opt. Mater.* 2018, 6 (22), 1800679.

73. Hou, H. Y.; Tian, S.; Ge, H. R.; Chen, J. D.; Li, Y. Q.; Tang, J. X., Recent 128

Progress of Polarization - Sensitive Perovskite Photodetectors. *Adv. Funct. Mater.* 2022, *32* (48), 2209324.

74. Zhan, Y.; Wang, Y.; Cheng, Q.; Li, C.; Li, K.; Li, H.; Peng, J.; Lu, B.;
Wang, Y.; Song, Y.; Jiang, L.; Li, M., A Butterfly - Inspired Hierarchical Light Trapping Structure towards a High - Performance Polarization - Sensitive Perovskite
Photodetector. *Angew. Chem., Int. Ed.* 2019, *58* (46), 16456-16462.

75. Song, Q.; Wang, Y.; Vogelbacher, F.; Zhan, Y.; Zhu, D.; Lan, Y.; Fang,
W.; Zhang, Z.; Jiang, L.; Song, Y.; Li, M., Moiré Perovskite Photodetector toward
High - Sensitive Digital Polarization Imaging. *Adv. Energy Mater.* 2021, *11* (29),
2100742.

76. Min, L.; Tian, W.; Cao, F.; Guo, J.; Li, L., 2D Ruddlesden-Popper Perovskite with Ordered Phase Distribution for High-Performance Self-Powered Photodetectors. *Adv. Mater.* **2021**, *33* (35), e2101714.

77. Qiu, J.; Zheng, Y.; Xia, Y.; Chao, L.; Chen, Y.; Huang, W., Rapid Crystallization for Efficient 2D Ruddlesden–Popper (2DRP) Perovskite Solar Cells. *Adv. Funct. Mater.* **2018**, *29* (47), 1806831.

78. Hoffman, J. M.; Strzalka, J.; Flanders, N. C.; Hadar, I.; Cuthriell, S. A.;
Zhang, Q.; Schaller, R. D.; Dichtel, W. R.; Chen, L. X.; Kanatzidis, M. G., In Situ
Grazing-Incidence Wide-Angle Scattering Reveals Mechanisms for Phase Distribution
and Disorientation in 2D Halide Perovskite Films. *Adv. Mater.* 2020, *32* (33), e2002812.
79. Liang, Y.; Shang, Q.; Wei, Q.; Zhao, L.; Liu, Z.; Shi, J.; Zhong, Y.;

129

Chen, J.; Gao, Y.; Li, M.; Liu, X.; Xing, G.; Zhang, Q., Lasing from Mechanically Exfoliated 2D Homologous Ruddlesden-Popper Perovskite Engineered by Inorganic Layer Thickness. *Adv. Mater.* **2019**, *31* (39), e1903030.

80. Xing, G.; Wu, B.; Wu, X.; Li, M.; Du, B.; Wei, Q.; Guo, J.; Yeow, E.
K. L.; Sum, T. C.; Huang, W., Transcending the slow bimolecular recombination in lead-halide perovskites for electroluminescence. *Nat. Commun.* 2017, *8* (1), 14558.

81. Wang, Z.; Wei, Q.; Liu, X.; Liu, L.; Tang, X.; Guo, J.; Ren, S.; Xing,
G.; Zhao, D.; Zheng, Y., Spacer Cation Tuning Enables Vertically Oriented and
Graded Quasi - 2D Perovskites for Efficient Solar Cells. *Adv. Funct. Mater.* 2020, *31*(5), 2008404.

82. Wang, Y.; Wang, P.; Zhou, X.; Li, C.; Li, H.; Hu, X.; Li, F.; Liu, X.;
Li, M.; Song, Y., Diffraction - Grated Perovskite Induced Highly Efficient Solar Cells
through Nanophotonic Light Trapping. *Adv. Energy Mater.* 2018, *8* (12), 1702960.

83. Cao, F.; Tian, W.; Wang, M.; Cao, H.; Li, L., Semitransparent, Flexible, and Self - Powered Photodetectors Based on Ferroelectricity - Assisted Perovskite Nanowire Arrays. *Adv. Funct. Mater.* **2019**, *29* (24), 1901280.

84. Li, B.; Huang, X.; Wu, X.; Zuo, Q.; Cao, Y.; Zhu, Q.; Li, Y.; Xu, Y.;
Zheng, G.; Chen, D.; Zhu, X. H.; Huang, F.; Zhen, H.; Hou, L.; Qing, J.; Cai,
W., High - Performing Quasi - 2D Perovskite Photodetectors with Efficient Charge
Transport Network Built from Vertically Orientated and Evenly Distributed 3D - Like
Phases. *Adv. Funct. Mater.* 2023, *33* (28), 2300216.

85. Hsiao, Y. W.; Cheng, B. S.; Hsu, H. C.; Wu, S. H.; Wu, H. T.; Leu, C. C.; Shih, C. F., Vertical - type 3D/Quasi - 2D n - p Heterojunction Perovskite Photodetector. *Adv. Funct. Mater.* **2023**, *33* (21), 2300169.

86. Loi, H. L.; Cao, J.; Guo, X.; Liu, C. K.; Wang, N.; Song, J.; Tang, G.; Zhu, Y.; Yan, F., Gradient 2D/3D Perovskite Films Prepared by Hot-Casting for Sensitive Photodetectors. *Adv Sci* **2020**, *7* (14), 2000776.

87. Liu, J.; Leng, J.; Wu, K.; Zhang, J.; Jin, S., Observation of Internal Photoinduced Electron and Hole Separation in Hybrid Two-Dimentional Perovskite Films. *J. Am. Chem. Soc.* **2017**, *139* (4), 1432-1435.

88. Wei, S.; Wang, F.; Zou, X.; Wang, L.; Liu, C.; Liu, X.; Hu, W.; Fan,
Z.; Ho, J. C.; Liao, L., Flexible Quasi-2D Perovskite/IGZO Phototransistors for
Ultrasensitive and Broadband Photodetection. *Adv Mater* 2020, *32* (6), e1907527.

Fang, H.; Hu, W., Photogating in Low Dimensional Photodetectors. Adv. Sci. 2017,
 4 (12), 1700323.

90. Wang, Z.; Gan, J.; Liu, X.; Shi, H.; Wei, Q.; Zeng, Q.; Qiao, L.; Zheng,
Y., Over 1 μm electron-hole diffusion lengths in CsPbI2Br for high efficient solar cells. *J. Power Sources* 2020, 454.

91. Zhang, J.; Zhao, J.; Zhou, Y.; Wang, Y.; Blankenagel, K. S.; Wang, X.;
Tabassum, M.; Su, L., Polarization - Sensitive Photodetector Using Patterned
Perovskite Single - Crystalline Thin Films. *Adv. Opt. Materi.* 2021, 9 (17), 2100524.

92. Wang, J.; Gudiksen, M. S.; Duan, X.; Cui, Y.; Lieber, C. M., Highly Polarized

Photoluminescence and Photodetection from Single Indium Phosphide Nanowires. Science 2001, 293 (5534), 1455-1457.

93. Zhang, J.; Zhao, J.; Zhou, Y.; Wang, Y.; Blankenagel, K. S.; Wang, X.;
Tabassum, M.; Su, L., Polarization - Sensitive Photodetector Using Patterned
Perovskite Single - Crystalline Thin Films. *Adv. Opt. Mater.* 2021, *9* (17), 2100524.

94. Lim, S.; Ha, M.; Lee, Y.; Ko, H., Large-Area, Solution-Processed, Hierarchical MAPbI3

Nanoribbon Arrays for Self-Powered Flexible Photodetectors. *Adv. Opt. Mater.* **2018**, *6* (21), 1800615.

95. Ji, C.; Dey, D.; Peng, Y.; Liu, X.; Li, L.; Luo, J., Ferroelectricity-Driven Self-Powered Ultraviolet Photodetection with Strong Polarization Sensitivity in a Two-Dimensional Halide Hybrid Perovskite. *Angew. Chem., Int. Ed.* **2020**, *59* (43), 18933-18937.

96. Li, Y.; Yang, T.; Xu, Z.; Liu, X.; Huang, X.; Han, S.; Liu, Y.; Li, M.;
Luo, J.; Sun, Z., Dimensional Reduction of Cs(2) AgBiBr(6) : A 2D Hybrid Double
Perovskite with Strong Polarization Sensitivity. *Angew. Chem., Int. Ed.* 2020, *59* (9),
3429-3433.

97. Zhang, W.; Hong, M.; Luo, J., Centimeter-Sized Single Crystal of a One-Dimensional Lead-Free Mixed-Cation Perovskite Ferroelectric for Highly Polarization Sensitive Photodetection. *J. Am. Chem. Soc.* **2021**, *143* (40), 16758-16767.

98. Yang, F.; Li, K.; Fan, M.; Yao, W.; Fu, L.; Xiong, C.; Jiang, S.; Li, D.; 132

Xu, M.; Chen, C.; Zhang, G.; Tang, J., Strongly Anisotropic Quasi - 1D BaTiS3 Chalcogenide Perovskite for Near - Infrared Polarized Photodetection. *Adv Opt Mater* **2022**, *11* (5), 2201859.

99. Ma, J.; Wang, H.; Li, D., Recent Progress of Chiral Perovskites: Materials, Synthesis, and Properties. *Adv Mater* **2021**, *33* (26), e2008785.

100. Ahn, J.; Ma, S.; Kim, J. Y.; Kyhm, J.; Yang, W.; Lim, J. A.; Kotov,
N. A.; Moon, J., Chiral 2D Organic Inorganic Hybrid Perovskite with Circular
Dichroism Tunable Over Wide Wavelength Range. *J Am Chem Soc* 2020, *142* (9), 4206-4212.

101. Yao, B.; Wei, Q.; Yang, Y.; Zhou, W.; Jiang, X.; Wang, H.; Ma, M.;
Yu, D.; Yang, Y.; Ning, Z., Symmetry-Broken 2D Lead-Tin Mixed Chiral Perovskite
for High Asymmetry Factor Circularly Polarized Light Detection. *Nano Lett* 2023, *23*(5), 1938-1945.

102. Liu, Q.; Wei, Q.; Ren, H.; Zhou, L.; Zhou, Y.; Wang, P.; Wang, C.; Yin, J.; Li, M., Circular polarization-resolved ultraviolet photonic artificial synapse based on chiral perovskite. *Nat Commun* **2023**, *14* (1), 7179.

103. Lu, Y.; Wang, Q.; Chen, R.; Qiao, L.; Zhou, F.; Yang, X.; Wang, D.;
Cao, H.; He, W.; Pan, F.; Yang, Z.; Song, C., Spin - Dependent Charge Transport
in 1D Chiral Hybrid Lead - Bromide Perovskite with High Stability. *Advanced Functional Materials* 2021, 31 (43), 2104605.

104. Lu, H.; Wang, J.; Xiao, C.; Pan, X.; Chen, X.; Brunecky, R.; Berry, 133
J. J.; Zhu, K.; Beard, M. C.; Vardeny, Z. V., Spin-dependent charge transport through 2D chiral hybrid lead-iodide perovskites. *Sci Adv* **2019**, *5* (12), eaay0571.

105. Long, G.; Jiang, C.; Sabatini, R.; Yang, Z.; Wei, M.; Quan, L. N.;
Liang, Q.; Rasmita, A.; Askerka, M.; Walters, G.; Gong, X.; Xing, J.; Wen,
X.; Quintero-Bermudez, R.; Yuan, H.; Xing, G.; Wang, X. R.; Song, D.;
Voznyy, O.; Zhang, M.; Hoogland, S.; Gao, W.; Xiong, Q.; Sargent, E. H., Spin
control in reduced-dimensional chiral perovskites. *Nat Photonics* 2018, *12* (9), 528-533.
106. Lu, H. P.; Wang, J. Y.; Xiao, C. X.; Pan, X.; Chen, X. H.; Brunecky,
R.; Berry, J. J.; Zhu, K.; Beard, M. C.; Vardeny, Z. V., Spin-dependent charge
transport through 2D chiral hybrid lead-iodide perovskites. *Sci Adv* 2019, *5* (12),
eaay0571.

107. Liu, J.; Leng, J.; Wu, K.; Zhang, J.; Jin, S., Observation of Internal Photoinduced Electron and Hole Separation in Hybrid Two-Dimentional Perovskite Films. *J Am Chem Soc* **2017**, *139* (4), 1432-1435.

108. Liu, D.; Wei, Q.; Zhuang, L.; Liu, M.; Zeng, L.; Ren, H.; Li, M.;
Lau, S. P., Nanoimprinted Quasi - 2D Perovskites toward High - Performance
Polarization - Sensitive Photodetectors. *Adv Opt Mater* 2024, *12*(11), 2302411.

109. Peng, Y.; Liu, X.; Li, L.; Yao, Y.; Ye, H.; Shang, X.; Chen, X.; Luo,
J., Realization of vis-NIR Dual-Modal Circularly Polarized Light Detection in Chiral
Perovskite Bulk Crystals. *J Am Chem Soc* 2021, *143* (35), 14077-14082.

110.Dang, Y.; Liu, X.; Cao, B.; Tao, X., Chiral halide perovskite crystals for 134

optoelectronic applications. Matter 2021, 4 (3), 794-820.

111.Zhao, R.; Guo, L.; Zhu, H.; Zhang, T.; Li, P.; Zhang, Y.; Song, Y., Regulation of Quantum Wells Width Distribution in Quasi-2D Perovskite Films for High-Performance Photodetectors. *Adv Mater* **2023**, *35* (25), e2301232.

112.Zhu, T.; Bie, J.; Ji, C.; Zhang, X.; Li, L.; Liu, X.; Huang, X. Y.; Fa,
W.; Chen, S.; Luo, J., Circular polarized light-dependent anomalous photovoltaic
effect from achiral hybrid perovskites. *Nat Commun* 2022, *13* (1), 7702.

113.Zhao, Y.; Yin, X.; Gu, Z.; Yuan, M.; Ma, J.; Li, T.; Jiang, L.; Wu, Y.; Song, Y., Interlayer Polymerization of 2D Chiral Perovskite Single - Crystal Films toward High - Performance Flexible Circularly Polarized Light Detection. *Advanced Functional Materials* **2023**, *33* (50), 2306199.

114.Wu, W.; Li, L.; Li, D.; Yao, Y.; Xu, Z.; Liu, X.; Hong, M.; Luo, J., Tailoring the Distinctive Chiral - Polar Perovskites with Alternating Cations in the Interlayer Space for Self - Driven Circularly Polarized Light Detection. *Adv Opt Mater* **2022**, *10* (18), 2102678.

115.Zhu, T.; Zhang, K.; Ji, C.; Zhang, X.; Ye, H.; Zou, Y.; Luo, J., Multilayered Alternating-Cations-Intercalation Chiral Hybrid Perovskites with High Circular Polarization Sensitivity. *Small* **2022**, *18* (51), e2203571.

116.Gao, W.; Wei, Q.; Wang, T.; Xu, J.; Zhuang, L.; Li, M.; Yao, K.; Yu, S.
F., Two-Photon Lasing from Two-Dimensional Homologous Ruddlesden-Popper
Perovskite with Giant Nonlinear Absorption and Natural Microcavities. ACS Nano

2022, *16* (8), 13082-13091.

117.Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G.,
2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications. *J Am Chem Soc* 2015, *137* (24), 7843-50.

118. Yuan, M.; Quan, L. N.; Comin, R.; Walters, G.; Sabatini, R.; Voznyy, O.;
Hoogland, S.; Zhao, Y.; Beauregard, E. M.; Kanjanaboos, P.; Lu, Z.; Kim, D.
H.; Sargent, E. H., Perovskite energy funnels for efficient light-emitting diodes. *Nat Nanotechnol* 2016, *11* (10), 872-877.