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论文题目：The Role of Organic Carrier in Determining the Structural Dimensionality and Optoelectronic Properties of Perovskites

The Role of Organic Carrier in Determining the Structural Dimensionality and Optoelectronic Properties of Perovskites

Harry Haorui Zhu

Abstract

Organic-inorganic hybrid perovskites have gained significant attention, yet controlling their dimensionality via the assistance of organic carriers to improve optoelectronic properties remains a challenge. Herein, we report a facile strategy for synthesizing high-quality two-dimensional perovskite single crystals by a controlled cooling method. Dissolution of these crystals in HBr and N-Dimethylformamide (DMF, polar solvent) mixed solutions triggers a precise phase transformation. Notably, the difference in HBr concentration plays a significant role in the final product. Pure DMF leads to non-emissive three-dimensional CsPbBr_3 , while HBr containing solutions facilitate the formation of zero-dimensional Cs_4PbBr_6 with intense green emission. We unveil that the role of HBr extends beyond providing bromide ions; it catalyzes the hydrolysis of DMF, altering the chemical environment and driving the phase transition. The optimized sample achieves an exceptional photoluminescence quantum yield, attributed to the highly pure 0D structure and the effective removal of the organic cation during recrystallization. Furthermore, we demonstrate the application potential of this high-efficiency green emitter by fabricating a white light-emitting diode (WLED) with a wide color gamut covering 136% of the NTSC standard. This work provides profound insights into the role of organic carriers in

perovskite dimensionality control and presents a robust route towards designing highly luminescent materials for advanced photonic devices.

Keywords: Organic-inorganic Hybrid Perovskite, Phase Transformation Control, Multi-Dimensional Perovskite, Photoluminescence Quantum Yield, HBr-mediated Hydrolysis, White Light-Emitting Diode (WLED)

Table of Contents

Abstract	2
Keywords	3
Introduction	5
Experimental Section.....	6
Synthesis	6
Characterization	7
Results and Discussion	8
Further Application	12
Conclusion	14
References	16
Acknowledgement.....	17

Introduction

Organic–inorganic hybrid perovskites have emerged as a highly promising class of semiconducting materials due to their exceptional optoelectronic properties, including high absorption coefficients, tunable bandgaps, and outstanding charge-carrier mobility. Among them, two-dimensional perovskites, characterized by their multi-quantum-well structures, offer enhanced environmental stability and rich structural diversity, making them attractive for applications in photovoltaics, LEDs, and photodetectors. However, the inherent quantum and dielectric confinement effects in 2D perovskites often lead to inefficient exciton dissociation and limited luminescence efficiency, which hinders their practical application in high-performance optoelectronic devices.

Recent efforts have focused on modulating the dimensionality and composition of perovskite crystals to optimize their optical properties.^[1] In particular, the transformation from 2D to 0D perovskite structures has attracted considerable attention due to the strong quantum confinement and high photoluminescence quantum yield exhibited by 0D materials such as Cs₄PbBr₆. Nevertheless, achieving controlled phase transformation while maintaining high crystallinity and emission efficiency remains a significant challenge.^[2] Moreover, the role of organic cations in stabilizing the layered structure and mediating the transformation process is not yet fully understood.

In this work, we report the synthesis of high-quality 2D organic–inorganic hybrid perovskite (HDA)Cs₂Pb₃Br₁₀ single crystals via a controlled cooling method and

demonstrate a facile HBr-mediated dissolution-recrystallization strategy to achieve efficient phase transformation into 3D CsPbBr₃ and highly luminescent 0D Cs₄PbBr₆. The introduced hexamethylenediamine (HDA²⁺) cation not only templates the formation of a layered perovskite framework but also influences the intermediate coordination environment during dissolution. We systematically investigate the structural and optical properties of the derived phases, revealing a remarkable PLQY of 94% for the transformed Cs₄PbBr₆ sample. Furthermore, we elucidate the underlying mechanism of HBr-induced hydrolysis of DMF and its role in facilitating the structural transformation. Finally, we demonstrate the application of the high-purity green-emitting Cs₄PbBr₆ in a wide-gamut white LED, achieving excellent color rendition and efficiency. This study provides new insights into the design of organic–inorganic hybrid perovskites with tailored dimensionality and enhanced optoelectronic performance, offering a viable pathway toward advanced luminescent materials for display technologies.

Experimental section

Synthesis

(HDA)Cs₂Pb₃Br₁₀ single crystals were synthesized by the controlled cooling crystallization method, taking methodology reference from document [3]. Initially, 1 mmol Cs₂CO₃ and 2 mmol Pb(CH₃COO)₂·3H₂O were added into 12 mL HBr under vigorous stirring at 25 °C for 30 min to ensure complete reaction. Subsequently, 1 mmol 1,6-hexamethylenediamine was introduced into the homogeneous solution, followed by continuous stirring at 120 °C until a transparent solution was achieved.

The resulting solution was then subjected to a gradient cooling process from 80 °C to 25 °C at a controlled rate of 2 °C per day, yielding pale yellow block-shaped single crystals.

0.5g (HDA)Cs₂Pb₃Br₁₀ single crystals were respectively dissolved in the mixed solution of x% of HBr/DMF (x=0, 10, 20, 30, 40), and the obtained orange powder and yellow powders were respectively denoted as HD0, HD1, HD2, HD3, and HD4.

Characterization

Referring to methodology reference taken from document [4], Single crystal X-ray diffraction data was carried out by single-crystal X-ray diffractometer equipped with CCD-detector, graphite monochromator, and Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The empirical absorption corrections were using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structures were solved by the direct methods using package SHELXS and refined using the SHELXL program. Powder X-ray diffraction was employed to confirm the crystal structures of HDx (x=0, 1, 2, 3, 4) samples. Photoluminescence spectra were measured at room temperature by a fluorescence spectrometer, which is equipped with a microsecond flash lamp and a 450 W xenon lamp. The structural changes of the samples at different temperatures were analyzed using a Fourier transform infrared spectrometer, which has a scanning range of 1000 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ at room temperature. Raman spectroscopy of different HBr/DMF mixed solutions was performed using a HORIBA Scientific LabRAM HR Evolution spectrometer with a 785nm laser.

Result and discussion

After successfully preparing the Organic-inorganic hybrid perovskite (HDA) $\text{Cs}_2\text{Pb}_3\text{Br}_{10}$ by the cooling crystallization method, in order to verify the phase purity of single crystals, the obtained single crystals were ground into powder for XRD testing and compared with the simulated data. As shown in Fig. 1a, the prepared (HDA) $\text{Cs}_2\text{Pb}_3\text{Br}_{10}$ crystals have high crystallinity and phase purity. Fig. 1b illustrates the layered crystal structure, wherein the inorganic layer is composed of $[\text{PbBr}_6]$ octahedra sharing vertices, with Cs^+ ions occupying the cavities. The relatively larger organic HDA^{2+} cations are unable to integrate into the inorganic framework. Consequently, the inorganic framework forms a sandwich-like three-layered structure of $[\text{Cs}_2\text{Pb}_3\text{Br}_{10}]_\infty$ (infinitely repeating its structure) along the bc plane. The densely packed $[\text{Cs}_2\text{Pb}_3\text{Br}_{10}]_\infty$ layers exhibit strong interactions with the HDA^{2+} cations via $\text{N-H}\cdots\text{Br}^-$ hydrogen bonds formed with the terminal amino groups ($-\text{NH}_2$) of HDA^{2+} . Then the optical properties of (HDA) $\text{Cs}_2\text{Pb}_3\text{Br}_{10}$ crystals were studied by conducting ultraviolet-visible (UV) absorption spectra. As shown in Fig. 1c, the prepared crystal exhibits pronounced absorption across both the ultraviolet and green regions, with the absorption edge of approximately 550nm. The inserted diagram in Fig1.c shows the calculated band gap (E_g) of 2.32 eV.

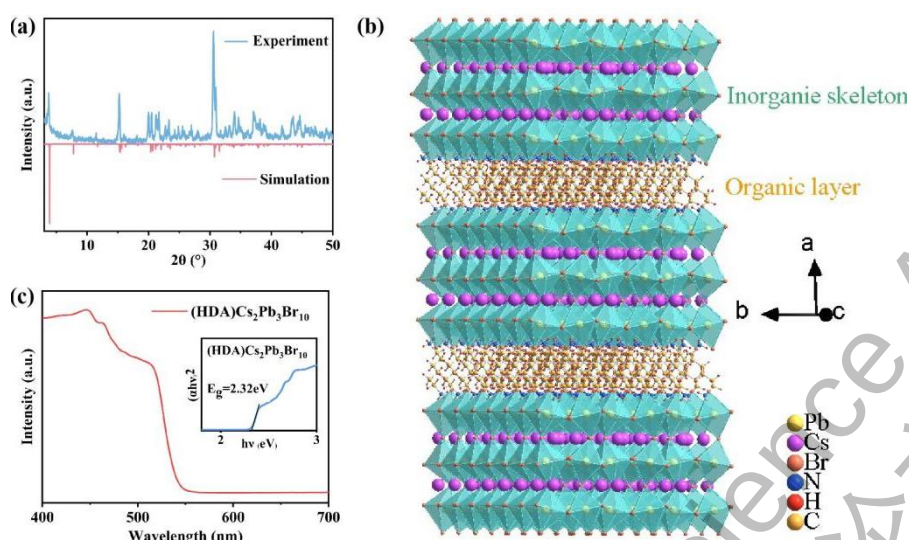


Fig. 1 (a) Experimental and calculated powder X-ray diffraction patterns of (HDA)Cs₂Pb₃Br₁₀ powdered sample; (b) Schematic of (HDA)Cs₂Pb₃Br₁₀ structure; (c) UV absorption spectrum for the (HDA)Cs₂Pb₃Br₁₀ powdered sample; inset shows the calculated optical Eg.

Dissolution of the single crystals in x% HBr/DMF mixed solutions ($x = 0, 10, 20, 30, 40$) revealed significant phase transformation and luminescence variations. As shown in Fig. 2a, the pure DMF system ($x = 0$) yielded orange non-emissive powder after antisolvent extraction, while HBr-containing systems produced yellow powders exhibiting intense green emission under UV excitation. XRD analysis (Fig. 2b) confirmed that HD0 corresponded to pure-phase CsPbBr₃, whereas HD1-HD4 matched perfectly with Cs₄PbBr₆, demonstrating HBr-induced transformation from 3D perovskite to zero-dimensional structure. PL characterization revealed that HD0 showed no detectable emission, while HD1-HD3 displayed strong emission centered at approximately 527 nm with minor peak position variations likely arising from differences in grain size distribution. In contrast, HD4 exhibited a blue-shifted emission peak at 520 nm with significantly reduced intensity, likely arising from

moisture-induced degradation of Cs_4PbBr_6 caused by excess HBr. According to the formula $(\alpha h\nu)^2 = A(h\nu - E_g)$ (where α is the absorbance coefficient, h is the Plank's constant, ν is the frequency, E_g is the bandgap), the bandgap width of 0-dimensional perovskite is approximately 2.3eV, and that of three-dimensional perovskite is 2.25eV. Remarkably, HD2 demonstrated an outstanding photoluminescence quantum yield of 94% (Fig. S2), highlighting the optimal HBr concentration for maximizing emission efficiency.

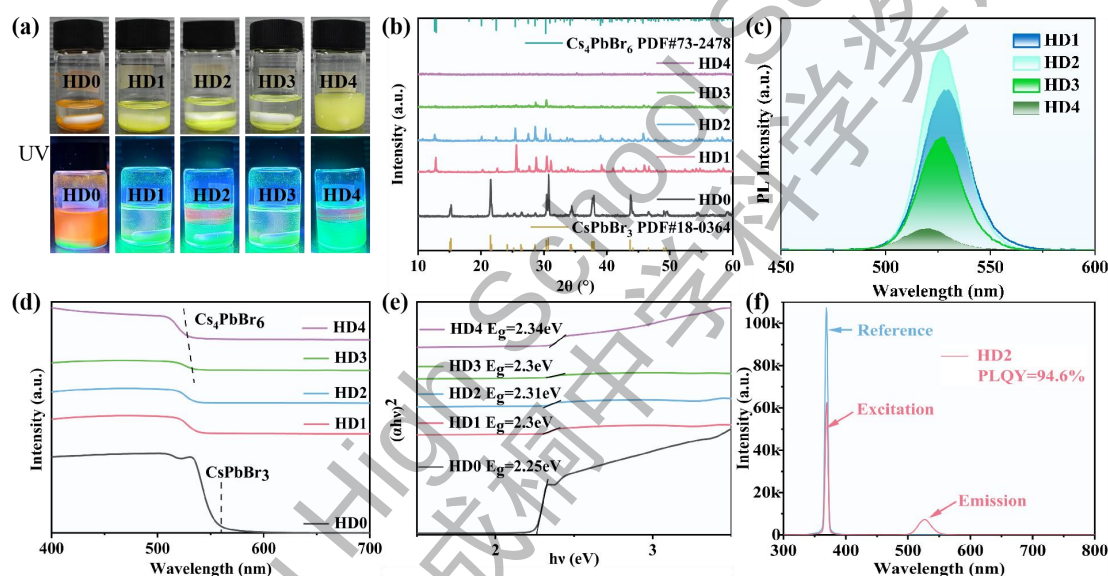
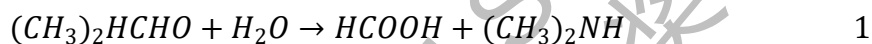


Fig2. HD0-HD4 samples: (a) Photographic images under daylight and UV light; (b) XRD patterns; (c) PL spectra; (d) Abs spectra; (e) band gap; (f) Quantum efficiency of HD2.

To study the phase transformation mechanism of 2D single crystals in organic solvents, the chemical environment of the single crystals was first investigated. For this purpose, Fourier (Fig. 3a) and Raman spectroscopy (Fig. 3b) were used to characterize the DMF/HBr mixed solution. In the Fourier infrared spectrum, it can be

seen that as the HBr content increases, the intensity of the characteristic peaks of DMF gradually weakens. Such as the C=O at 1682 cm⁻¹, the C-N at 1508 cm⁻¹, the (CH₃)N at 1093 cm⁻¹, and the C-H at 1383. New infrared peaks gradually appear. At 1022 cm⁻¹, 2475 cm⁻¹, and 3466 cm⁻¹. This result matches the Raman spectrum (as shown in Fig. 3b). DMF readily hydrolyzes under the catalysis of acid, so after adding the HBr solution, DMF hydrolyzes into formic acid and dimethylamine, as shown in Formula 1:



Then HBr protonates the dimethylamine obtained after hydrolysis to form dimethylamine bromide salt as shown in Formula 2. This phenomenon indicates that the solubility of DMF decreases and water exists in the chemical system.

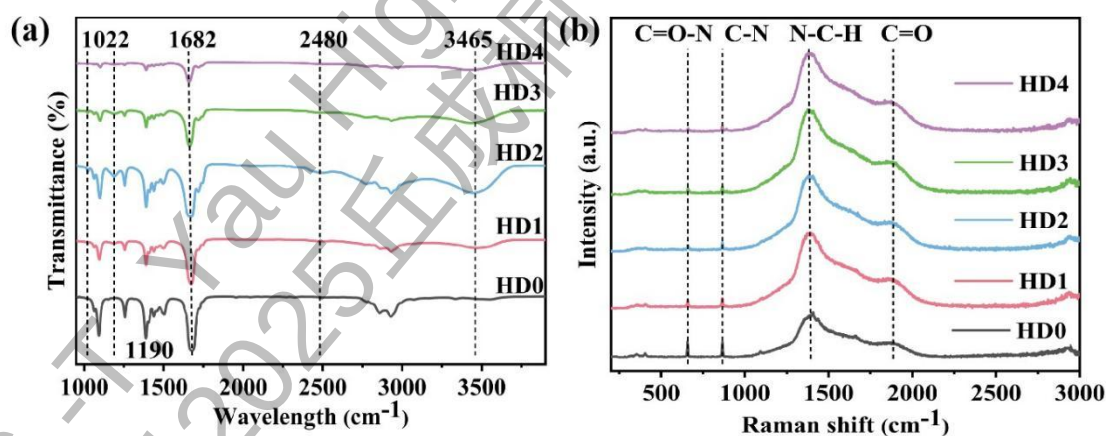
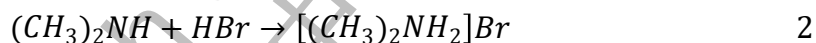


Fig. 3 (a) FTIR spectra of HD0-4 (b) Raman spectra of HD0-4.

Based on the previous analysis, when the Quasi-2D crystal is dissolved in the DMF organic solvent, Pb²⁺, Cs⁺, Br⁻ and HDA²⁺ all form intermediates with DMF. After extraction with toluene, the ions Cs⁺, Pb²⁺ and Br⁺ tend to form the structurally stable CsPbBr₃ crystals. However, the HDA²⁺ organic group does not have sufficient

energy to enter the stable 3D structure and remains only in the solution environment. When HBr solution is added to the DMF organic solvent, DMF undergoes hydrolysis to form formic acid and dimethylamine bromide salt. At this point, the solubility of the mixed solution decreases, and H₂O exists in the chemical environment. Therefore, when Quasi-2D recrystallizes into CsPbBr₃, due to the increase in Br⁻ concentration and hydrolysis, CsPbBr₃ further transforms into Cs₄PbBr₆.

Further Application

To demonstrate the application potential of the high efficiency Cs₄PbBr₆ in display backlight, a white light-emitting diode (WLED) device was fabricated. A 435nm GaN chip served as the blue light source, while Cs₄PbBr₆ and commercial K₂SiF₆: Mn⁴⁺ (KSF) powders acted as green and red light source. Fig. 6a displays the electroluminescence (EL) spectra of the packaged WLED under an driving current of 20mA, accompanied by photographs of the device before and during operating. The constructed WLED has a luminous efficiency of 98.04 lm W⁻¹ with a CIE color coordinates of (0.2908, 0.2955) and correlated color temperature of 8651K. Color-gamut performance was quantified by spectrally filtering the EL spectrum through commercial blue (B), green (G) and red (R) color filters, and the transmittance spectra of these filters are presented in Fig. 6b. The resulting filtered spectra, presented in Fig. 6c–e, delineate the RGB primaries and cove the color space of the 136 % NTSC and 101.6 % Rec. 2020 (Fig. 6f). Compared to the recently reported perovskite WLEDs (Table 1), the device constructed in this work exceeds

those for some critical parameters.

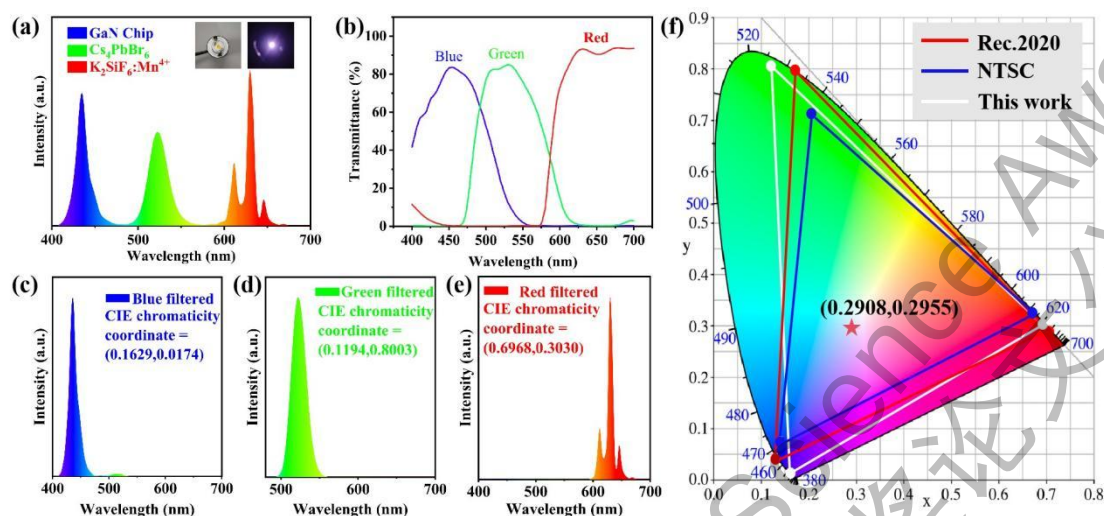


Fig. 6 (a) EL spectra of WLED (b) Transmittance spectra of commercial blue, green and red filters. (c)-(e) The corresponding EL spectra after filtering. (f) CIE color coordinate and color gamut of the WLED device working at 20 mA.

Table 1

Materials	CCT /K	Luminous efficiency/ lmW ⁻¹	Color gamut(NSTC/R ec.2020)	CIE coordinate	References
Rb2CuBr3: xMn	6011	110.31	114.2%/85.2%	(0.321,0.342)	[7]
CsPbX3@glass	-	25.8	-/127%	-	[5]
CsPbBr3 (CPB) QDs	-	-	122%/90%	(0.3323, 0.3342)	[6]
Cs4PbBr6	8651	98.04	136%/101.6%	(0.2908,0.2955)	This Article

Conclusion

In summary, we have successfully demonstrated a novel and efficient pathway for fabricating highly luminescent 0D Cs_4PbBr_6 through the HBr-mediated phase transformation of a tailor-made 2D organic-inorganic hybrid perovskite $(\text{HDA})\text{Cs}_2\text{Pb}_3\text{Br}_{10}$. The HDA^{2+} cation serves not only as a structural template for the initial layered crystal but also plays a crucial role in the subsequent dissolution. The recrystallization process selectively excluded HDA cations from the inorganic framework, thereby facilitating the formation of a pure 0D phase.

The concentration of HBr in the DMF solvent is identified as the critical parameter governing the phase transition outcome, determining a direct conversion from 2D to either non-emissive 3D CsPbBr_3 or highly emissive 0D Cs_4PbBr_6 . A comprehensive mechanistic study reveals that HBr catalyzes the hydrolysis of DMF, which alters the chemical equilibrium and provides a high-concentration bromide source, ultimately steering the recrystallization towards the thermodynamically favored Cs_4PbBr_6 . The optimized sample exhibits a remarkable green emission with a near-unity PLQY of 94%, which is among the highest values reported for this material, underscoring the effectiveness of our method in minimizing non-radiative recombination defects.

In addition, which worth specifically noticed in that, when the HBr concentration exceeds 20% (HD3, HD4), the PLQY shows a declining trend, and the emission peak of HD4 exhibits a blue shift (in which the wavelength shortened, the frequency lengthened). We attribute this to side reactions introduced by excess HBr. A high

concentration of HBr implies a significant increase in the water content within the system, and Cs_4PbBr_6 is relatively sensitive to moisture. Water molecules can etch the crystal lattice, inducing surface defects and non-radiative recombination centers, thereby leading to a decrease in luminescence efficiency. In relatively low HBr environment cases, Hbr plays the positive roles of providing high concentration of Br anions (to reach the 1:6 ratio required in stoichiometry), and provides the appropriate amount of dimethylamine salt generated from hydrolysis effectively assists in the formation of a perfect crystal lattice, thereby maximally reducing defects, which are the primary source of non-radiative recombination. Thus, a remarkably high PLQY of up to 94% was achieved. Meanwhile, an extremely acidic environment may also disrupt the crystal perfection. Fascinatingly could be found that, similar products of perovskite coincide with the percentage of 20% being the most effective luminescent percentage,^[7] which could provide another experimental evidence for the “why 20%” question. Hence, the 20% HBr concentration represents an optimum balance between providing an adequate bromine source and avoiding moisture-induced degradation.

Furthermore, the practical application of this high-performance green emitter was convincingly validated by the fabrication of a WLED device exhibiting an excellent luminous efficiency and a wide color gamut. This work not only provides a profound understanding of the role of organic carriers and solvent engineering in perovskite dimensionality control but also establishes a robust and scalable strategy for developing high-efficiency luminescent materials for next-generation display and lighting technologies.

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This project originated from habit of regularly reviewing and documenting academic journal literature, combined with interest in LED materials and next-generation photovoltaic technology. During the literature review process, we recognized that the strategic role of organic solvents in organic-inorganic hybrid low-dimensional perovskites is a hot research topic with room for further systematic investigation. Professor Zeng from East China University of Science and Technology, whom I contacted, endorsed our proposed direction and helped me refine the core scientific question: to systematically correlate specific organic carrier structures with their induced perovskite dimensionality and resulting optoelectronic properties. She to an important extent assisted me in designing experiments, developing experimental procedures, analyzing data, overcoming technical challenges, and interpreting results. Her expertise in perovskite materials and optoelectronics was crucial in defining our research direction and ensuring the scientific rigor of our work.

Meanwhile, my school tutor, Dr.Liu, devoted significant time to guiding me personally, in paper standardization, plenty of academic discussion, planning guidance, and fostering interest in scientific innovation. I am particularly grateful for their encouragement of critical thinking, which has been an invaluable learning experience for me. We hereby confirm that all guidance and supervision provided by both

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