Dominant Factors Limiting Optical Gain in Layered Two-Dimensional Halide Perovskite Thin Films†

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† Electronic supplementary information (ESI) available: Statistics of perovskite optical gain reports, typical lasing evidence, physical characterization (XRD, SEM and steady state absorption), damage threshold determination, effects of PMMA on PEPI PL spectrum, XPS surface composition ratio, parameters for the rate equations.

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ABSTRACT: Semiconductors are the ubiquitous gain media for coherent light sources. Solution-processed three-dimensional (3D) halide perovskites (e.g., CH₃NH₃PbI₃) with their outstanding room temperature optical gain properties is the latest member of this family. Their two-dimensional (2D) layered perovskite counterparts with natural multiple quantum well structures exhibit strong light-matter interactions and intense excitonic luminescence. However, despite such promising traits, there have been no reports on room temperature optical gain in 2D layered perovskites. Herein, we reveal the challenges towards achieving amplified spontaneous emission (ASE) in the archetypal (C₆H₅C₂H₄NH₃)₂PbI₄ (or PEPI) system. Temperature-dependent transient spectroscopy uncovers dominant free exciton trapping and bound biexciton formation pathways that compete effectively with biexcitonic gain. Phenomenological rate equation modeling predicts a large biexciton ASE threshold of ~1.4 mJ/cm², which is beyond the damage threshold of these materials. Importantly, these findings would rationalize the difficulties in obtaining optical gain in 2D perovskites and provide new insights and suggestions for overcoming these challenges.

Keywords: perovskite, lasing, amplified spontaneous emission, two dimensional, photoluminescence spectroscopy
Introduction

Organic-inorganic lead halide perovskites emerged as a technologically important semiconductor due to recent discoveries of their outstanding optoelectronic properties. They can be categorized based on their structural dimensionality, with 2D (A$_2$BX$_4$ formula) and 3D (ABX$_3$ formula) perovskite being the most studied materials. While disproportionate attention has been placed on 3D perovskites for photovoltaics, there has also been a recent surge of interests on their light emitting and optical gain properties. 2D perovskites had dominated the limelight in the past decades due to their potential for applications in light emitting diodes. Nonetheless, reports of optical gain in solution-processed 2D perovskite thin films are far and few between: out of 28 perovskite optical gain reports to date, there is only one early report by Kondo et al. that claimed 2D perovskite cavity lasing at 16 K (See Supplementary Information Fig. S1). Although this report showed evidence of narrow emission linewidth at higher pump intensity, the light-in-light-out data presented did not indicate a clear transition from spontaneous emission to stimulated emission. As Samuel et al. points out, lasing phenomenon should satisfy four criteria, namely: 1) narrow emission linewidth, 2) clear threshold associated with emission intensity and linewidth, 3) tunable light emission with laser cavity and gain medium, and 4) a beam-like output (See Supplementary Information Fig. S2). It is important to ensure that all these criteria are fulfilled to eliminate phenomena with similar signatures from luminescent microcavities and waveguiding effects that could be mistakenly assigned as lasing. As such, it is highly possible (in view of the limited data available from the manuscript) that the “lasing” reported by Kondo et al. could in fact be a case of a luminescent microcavity or waveguiding effect (or a combination of both). Although the possibility of attaining lasing from 2D perovskites cannot be totally ruled out, it is surprising that reports on optical gain from 2D
perovskites are scarcely reported. 2D perovskites (e.g., (C\textsubscript{6}H\textsubscript{5}C\textsubscript{2}H\textsubscript{4}NH\textsubscript{3})\textsubscript{2}PbI\textsubscript{4} (hereafter as PEPI)), which exhibits strong excitonic green emission, could be potential gain materials for overcoming the “green gap” in semiconductor lasers\textsuperscript{19}. Particularly, PEPI has been extensively investigated for light emission applications in the 1990s and early 2000\textsuperscript{13,14,20}. The naturally formed quantum well in 2D perovskite is also attractive for integration into electrically pumped gated green lasers\textsuperscript{21}. The excellent in-plane mobility experienced by charge carriers in the inorganic quantum well is also expected to be better than a four-level conjugated organic semiconductor systems which exhibit ASE\textsuperscript{22}. Unfortunately, the limited reports on 2D perovskite lasing clearly unpins the challenges in achieving optical gain from these materials. Detailed photophysical insights on the relaxation processes of the photoexcited species, as well as the dominant factors limiting optical gain, are therefore urgently required.

Herein, we present a detailed photophysical study on solution-processed PEPI thin film using temperature and pump-fluence dependent photoluminescence (PL) spectroscopy. Room temperature PL spectroscopy using high laser pump fluence (of the order of 100 \(\mu\)J/cm\(^2\)) revealed a dominating free excitonic emission peak (peak 1) with a notable absence of ASE. Low temperature PL revealed a more significant bound excitonic emission peak (peak 2) with a third biexcitonic emission peak (peak 3) appearing at higher laser excitation fluence (~30 \(\mu\)J/cm\(^2\)). Nonetheless, no optical gain (i.e., ASE) can be observed from PEPI at low temperatures using high laser fluence (of the order of 100 \(\mu\)J/cm\(^2\)). Arrhenius plot from the temperature dependent PL revealed a small energy difference (~10 meV) between peak 1 and 2 emission level and suggests dependencies between these levels. Significant PL quenching of peaks 2 and 3 upon surface passivation of PEPI points to a surface origin of these two peaks. Importantly, our findings shed light on the interplay between competing relaxation channels in PEPI, which could
potentially limit biexcitonic ASE in PEPI. This limitation concurs with theoretical modeling which shows a large biexcitonic ASE threshold beyond damage threshold of PEPI. From these findings, we provided suggestions for overcoming optical gain challenges in 2D perovskites.

**Experimental**

**Thin Film Fabrication.**

All the chemicals were purchased from Sigma-Aldrich. C₆H₅C₂H₄NH₃I was prepared by adding 5.45 ml of HI (57 %) to the mixture of 5 g of C₆H₅C₂H₄NH₂I and 5 ml of methanol at 0° C. The reaction mixture was further stirred for an hour at room temperature. Excess solvent was then removed using the rotary evaporator at 50° C to obtain a white powder mass. The powder was then washed with cold ether for several times and dried to obtained C₆H₅C₂H₄NH₃I powder. PEPI solution was subsequently obtained by dissolving stoichiometric amounts (2:1) of C₆H₅C₂H₄NH₃I and PbI₂ in N, N-dimethylformamide. The weight concentration of this solution was fixed at 25 wt% for PL measurements. Two samples are fabricated for PL measurements. The first sample was fabricated by spincoating the solution on a cleaned quartz substrate at 4000 rpm and 30 seconds. The resulting film was subsequently annealing at 100 °C for 30 minutes. The second sample was fabricated by spincoating an additional PMMA (10 mg/mL in chloroform) layer on the perovskite film and subsequently annealing it at 100 °C for 15 minutes. Both samples are fabricated in glovebox filled with inert nitrogen gas.

**Low Temperature Steady-State and Time-Resolved Photoluminescence Spectroscopy**

Femtosecond excitation pulses (wavelength, 400 nm) were obtained via second harmonic generation of pulses from a Coherent Libra regenerative amplifier (1 KHz, 50 fs), which was seeded by a Coherent Vitesse oscillator. The samples were mounted in a cryostat and cooled
using a continuous flow cryocooler (CRYO Industries) feed with helium gas (99.9997% purity, Air Products). For steady-state PL spectroscopy, the backscattered PL emission was collected and dispersed using a 600 g/mm spectrometer (Princeton Instruments). For TRPL spectroscopy, the backscattered PL emission was collected and dispersed using a 600 g/mm spectrometer (Princeton Instruments) and temporally resolved using an Optronis streak camera system (~10 ps resolution).

**Steady-State Absorption Spectroscopy**

UV-Vis absorption spectrum was collected with a Shimadzu UV3600 spectrophotometer. The sample absorbance is scanned from 280 nm to 900 nm with 1 nm interval. The reference absorbance spectrum for quartz substrate is also collected to correct for any contributions from it.

**X-ray Photoelectron Spectroscopy (XPS)**

XPS was performed using a home-built UHV multi-chamber system with base pressure at least 1 \( \times 10^{-9} \) torr (~10⁻⁷ Pa). The perovskite is grown on an indium tin oxide substrate and excited using photon energy of 1486.7 eV. The X-ray photons originate from a monochromatic Al K\( _a \) source while the ejected photoelectrons are measured by an Omicron EA125 electron analyzer.

**X-ray Diffraction (XRD) Spectroscopy**

XRD was performed to identify structural and phase properties of the PEPI thin film. The XRD pattern was recorded using Bruker AXS (D8 ADVANCE) X-ray diffractometer using a Cu K\( _\alpha \) radiation source with 2\( \theta \) from 0° to 90°.
Results and discussion

Power dependent PL characterizations. The structure of PEPI consists of alternating organic (C₆H₅C₂H₄NH₃⁺) and inorganic layers (PbI₆⁴⁻ octahedron), forming quantum wells that strongly confine excitons in the inorganic part – Fig. 1a. The self-assembled layered structure, which can be easily obtained via spin coating, is confirmed using XRD (See Supplementary Information Fig. S3a). The spin coated film is also shown to possess good substrate coverage and sample morphology (See Supplementary Information Fig. S3b). A strong excitonic absorption peak, arising from dielectric confinement in PEPI, can be seen in the steady-state absorption spectrum. The strong excitonic behavior also results in a large exciton binding energy of ~180 meV (See Supplementary Information Fig. S3c). Correspondingly, a strong excitonic emission peak (peak 1: ~ 525 nm) could be observed at room temperature in the PL spectrum – Fig. 1b. The room temperature laser fluence dependent PL spectrum clearly shows the absence of ASE in PEPI, even at high laser fluence. In the low temperature regime (i.e., 10 K), where ASE threshold is expected to be lower, ASE is still not observed and only three spontaneous emission peaks are observed (peak 1, peak 2: ~ 535 nm and peak 3: ~545nm) – Fig. 1c. Although peak 3 becomes more intense with increasing laser fluence, no superlinear increase in PL intensity (characteristic of ASE) could be observed. In both room and low temperature PL measurements, the measurements were stopped at laser fluence just below damage threshold. Here, the damage threshold using 400 nm excitation is of the order 100 µJ/cm² or 10¹⁹ cm⁻³ incident photon density, beyond which the sample is damaged irrevocably and the PL emission diminishes (See
Supplementary Information Fig. S4). These studies demonstrate and affirm the difficulties in obtaining ASE from PEPI at both room- and low-temperatures.

**PL Peak Assignments.** Prior to modeling the recombination kinetics in PEPI, we need to establish the identities of peak 1, 2 and 3 (See Fig. 1c). The identity of peak 1 is well-established to originate from free exciton recombination. The energy of peak 1 remains almost unchanged with a slight unconventional red shift with decreasing temperature – Fig. 2a. The red shifting behavior, which has previously been observed in 3D perovskite, can be attributed to effects from negative Varshni parameter\(^23\). Unfortunately, the origins of peak 2 and 3 are still a matter of debate in the literature.

For peak 2, its origins were either attributed to a phonon replica or to bound excitons. Gauthron *et al.*\(^{24}\) observed two low temperature PL peaks (peak 1 and peak X (2.337 eV or 530.5 nm, which is not observed by us)) and found a significant interaction between the free excitons (peak 1) and optical phonons from their phenomenological model. From the established relation between peak 1 and peak X, they attributed peak X to be a phonon replica of peak 1. Peak X (at 530.5 nm) observed by Gauthron *et al.* at 10K need not correspond to peak 2 (535nm) in our study. Furthermore, peak X also lacks the characteristic features of phonon replicas. On the other hand, Hong *et al.*\(^{25}\) observed multiple evenly spaced peaks (phonon replicas) at 2 K that are red-shifted from peak 1. However, Kitazawa *et al.*\(^{26}\) attributed a bound exciton origin to peak 2. They found a large characteristic exciton binding energy (~200 meV) for (C\(_6\)H\(_5\)C\(_2\)H\(_4\)NH\(_3\))\(_2\)PbI\(_4\) as well as a much smaller binding energy of ~10 meV, which they attributed to the trapping-detrapping energy for bound exciton. This small energy is equivalent to a temperature of ~120 K and corresponds well to the temperature at which peak 2 becomes prominent. These latter findings are consistent with our observations – Fig. 2b and 2c. In addition, the decay rate for peak 1 and 2
(Fig. 2d) are different and this suggests that peak 2 is unlikely to be a phonon replica of peak 1. The bound exciton origin for this red-shifted peak was also evident in a similar 2-D perovskite \(((\text{C}_{10}\text{H}_{21}\text{NH}_{3})_{2}\text{PbI}_{4})^{27}\). Next, significant quenching of peak 2 at low temperatures (77 K and 10 K - See Supplementary Information Fig. 5a, 5b) is also observed after depositing a layer of PMMA on top on PEPI. The variable degree of surface quenching for different sample batches at 77 K (See Supplementary Information Fig. S5b) suggests large surface trap contribution to peak 2 with some bulk trap contribution - implying the significant presence of surface bound excitons. The passivation of surface traps on PEPI by PMMA is consistent with the broadening of peak 1 \((\text{i.e.},\) free exciton peak), an PL intensity increase by \(\sim 37\%\) and free exciton lifetime lengthening at \(\sim 10\) K (See Supplementary Information Fig. S5a, S5c and S5d respectively). X-ray photoelectron spectroscopy (XPS) revealed the presence of organic surface vacancies in PEPI (See Supplementary Information Fig. S6 and Table S1), which may be responsible for the surface traps in PEPI. These findings suggest that surface traps in PEPI cannot be neglected and could potentially have an adverse effect on optical gain.

For peak 3 that appears at high excitation fluence, Shimizu \textit{et al.} attributed the emission to originate from tri-excitons based on the 2.5 proportionality relation\textsuperscript{28,29} between the emission intensity and excitation fluence. However, based on the quadratic increase in peak 3 emission with laser fluence at low temperatures, our result suggests a biexcitonic origin to peak 3 (See Supplementary Information Fig. S7). Such biexcitonic emission have also been previously reported for \((\text{C}_{6}\text{H}_{13}\text{NH}_{3})_{2}\text{PbI}_{4}\)\textsuperscript{17}. The biexcitons in PEPI, with a binding energy of 40 meV (See Supplementary Information for biexciton binding energy determination), are more likely to reside at the surface as bound biexciton since peak 3 is suppressed with significant quenching of peak 2 (See Supplementary Information Fig. S8).
In summary, our findings show that peak 1 originates from free excitons; peak 2 arises from surface bound excitons, and peak 3 from surface bound biexcitons.

**Theoretical modeling of charge carrier relaxation.** To investigate the factors affecting ASE in PEPI, we developed a model for carrier and emission dynamics in PEPI. This model is modified based on a well-established model of ASE in semiconductor nanostructures to account for our peak assignment. A schematic of the model is shown in Fig. 3a below, which comprises of three emissive levels: free exciton, bound exciton and bound biexciton level. This model involves the following processes: excitation to the free carrier band $|C\rangle$, which (1) relax towards the free exciton $|X\rangle$ and bound exciton $|X_B\rangle$ level, (2) capture of free exciton to bound exciton, (3) non-radiative relaxation channel of free and bound exciton, (4) emission of free exciton, (5) emission of bound exciton, (6) formation and emission of bound biexciton $|XX_B\rangle$ and (7) non-radiative exciton-exciton annihilation process. These processes are illustrated in Fig. 3a. From this model, the dynamics of the system are described by the following rate equations:

\[
\frac{N_C}{dt} = \frac{\alpha_F}{\tau_L \sqrt{\pi \hbar \omega}} \exp \left(-\frac{t^2}{\tau_L^2}\right) - \frac{N_C}{\tau_{CX}} - \frac{1}{2} \gamma (N_X^2 + N_{X_a}^2) + \frac{N_C}{\tau_{CX_a}} \exp \left(-\frac{t^2}{\tau_L^2}\right) \tag{1}
\]

\[
\frac{N_X}{dt} = \frac{N_C}{\tau_{CX}} - k_{X_{nr}} N_X - \frac{N_X}{\tau_{Xr}} - v_{gX} g_X S_X - C_X N_X - \gamma N_X^2 \tag{2}
\]

\[
\frac{N_{X_a}}{dt} = \frac{N_C}{\tau_{CX_a}} + C_X N_X - k_{X_{nr}} N_{X_a} - \frac{N_{X_a}}{\tau_{X_{ar}}} - v_{gX} g_{X_a} S_{X_a} - \gamma N_{X_a}^2 - \frac{B_{XX_a} N_{X_a}^2}{\tau_{XX_{ar}}} - v_{gXX_a} g_{XX_a} S_{XX_a} \tag{3}
\]

\[
\frac{S_X}{dt} = +v_{gX} g_X S_X + \frac{N_X}{\tau_{Xr}} \tag{4}
\]

\[
\frac{S_{X_a}}{dt} = +v_{gX} g_{X_a} S_{X_a} + \frac{N_{X_a}}{\tau_{X_{ar}}} \tag{5}
\]
\[
\frac{S_{xx}^{x}}{dt} = +v_{g_{xx}^{x}g_{xx}^{x}S_{xx}^{x}} + \frac{B_{xx}^{x}N_{xx}^{2}}{\tau_{xx}^{x}}
\]  

(6)

The descriptions of the terms in equation (1) to (6) are listed in Table 1. Meanwhile, the optical gain \((g)\) is modeled by the competition between the absorption and stimulated emission:

\[
g_{X} = g_{X0}(2N_{X} / D_{X} -1) 
\]  

(7)

\[
g_{x_{b}} = g_{x_{b}0}(2N_{x_{b}} / D_{X} -1) 
\]  

(8)

\[
g_{xx_{b}} = g_{xx_{b}0}(2B_{xx_{b}}N_{xx_{b}}^{2} / D_{X} -1)
\]  

(9)

Here, the initial gain \(i.e., g_{X0}, g_{x_{b}0} \) and \(g_{xx_{b}0} \) used are obtained from the linear absorption coefficient measurement, since gain = −absorption when \(N = 0\). The density of states \(D_{X} \) is estimated by the density of valence electrons of lead cation, which is the main contributor for the valence states. The parameters used in this model are either taken from experimental parameter or obtained from experimental data (See Supplementary Information Table S2 for the parameters). The free exciton lifetime (peak 1) from the pristine PEPI film can well-fitted with the numerical solution of equation (3) – Fig 4b. We also found that the numerical solution of equation (1) to (3) as a function of laser pump fluence can be well-fitted by the deconvolved PL integrated intensity for the respective peaks – Fig 3c. Our model also predicts an absence of ASE in the pump fluence range used in our studies – consistent with our experimental data. The behavior of the respective peaks is also extrapolated to regime above the damage threshold.
(above the laser fluence range used) – Fig 3c inset. Our model predicts an ASE onset for peak 3 at a laser fluence of 1.4 mJ/cm^2 originating from biexcitonic ASE in PEPI. This value is approximately 1 order of magnitude higher than the experimental damage threshold. Here, we also explored the possibility of single excitonic gain\(^3\). While single excitonic gain in caesium lead halide perovskite QDs\(^9\) and in CdSe-based\(^3\) colloidal quantum dots have previously been proposed, such single excitonic ASE onsets are not experimentally observed for peak 1 (free exciton) and peak 2 (bound exciton) in the PEPI system. This is understandable from the model that the dominant competing relaxation channels in PEPI (\textit{i.e.}, free exciton to bound exciton relaxation and bound exciton to bound biexciton relaxation) would not favor the formation of metastable states. These competing channels are pre-requisites for the bound biexciton formation and for the subsequent bound biexciton gain buildup. Such competing channels are also not representative of a four-level lasing system found in excitonic organic semiconductors gain media\(^2\).

**Proposed solutions to overcome the optical gain challenges.** While AlInGaP and GaN materials have made electrically pumped red and blue lasers possible, a suitable candidate for green lasers is still elusive\(^1\). Thus, overcoming of green gap in lasing still remains an important research area. If a suitable candidate is found, this could mean a huge breakthrough in the photonics industry. Conventional green lasing generated by frequency-doubling using a nonlinear crystal could then be replaced by a more efficient, directly generated green laser. In addition, high quality red, green and blue laser-based display\(^3\) could also be made possible. Solution processed 2D perovskite systems exhibiting strong optically and electrically pumped spontaneous green emission could possibly contribute to realization of electrically pumped green laser. However, achieving optical gain with these 2D materials have proven challenging. From
the literature reports and our experimental results, we propose several key factors that may help to overcome the optical gain problem in 2D perovskite.

Managing exciton recombination losses is an important factor for achieving optical gain in 2D perovskite. From PL measurements, we establish that there are significant surface traps in PEPI. These surface traps give rise to the formation of bound excitons (from free exciton) and bound biexcitons (from bound excitons). These competing pathways could be one of reasons behind the lack of optical gain from biexcitons (formed directly by free excitons). As shown from our theoretical modeling, only bound biexcitonic gain can be achieved from this system. Unfortunately, this also means that these competing relaxation channels present cannot be eliminated for bound biexciton formation. These channels could act as losses and account for the high bound biexcitonic ASE threshold of 1.4 mJ/cm² calculated. A possible way to reduce loss and lower ASE/lasing threshold would be to introduce a ultrahigh quality laser cavity (See Figure 4a).

Enhancing excitonic gain through the use of 2D perovskite nanocrystals to induce optical gain could also be explored. Typical nanocrystals gain involves at least two excitons (biexciton), but the formation of biexcitons at high laser fluence can promote non-radiative Auger recombination. Klimov et al.31 had previously proposed a type-II core/shell configuration which employs carrier-induced Stark effect to induce single exciton gain and eliminate Auger recombination. Carrier-induced Stark effect breaks the symmetry between absorption and emission by confining opposite charges in core and shell respectively and thereby making population inversion of single exciton possible. Similarly, a semiconductor shell surrounding 2D perovskite nanocrystals (core) can be used (See Figure 4b). Building on this idea and careful choice of organic component (R), a 2D perovskite thin film with type II electronic
configuration\textsuperscript{34} could also be fabricated (See Figure 4c) and may be useful for achieving single exciton gain. From our XPS data, the defects in PEPI were found to be from C and N deficiencies that could possibly originate from C-N bond breakage in the organic compound. Therefore using an organic component with a larger C-N bond dissociation energy may be helpful for traps reduction. Instead of using a (R-NH\textsubscript{3})PbI\textsubscript{4} structure where van der Waals forces exists between two ammonium units, a covalently bonded ammonium units structure with formula (NH\textsubscript{3}-R-NH\textsubscript{3})PbI\textsubscript{4}\textsuperscript{34} (See Figure 4d) would be helpful. Strong covalently bonded constituents could lead a better film morphology which can results in further traps reduction\textsuperscript{35}.

\textbf{Conclusion}

In retrospect, ultrafast spectroscopy provides a powerful means to probe exciton relaxation in PEPI. Regardless of excitation at low or room temperature, no ASE could be observed in spin-coated PEPI thin film. Formation and relaxation of free, bound and biexciton were found to be very dependent on each other. Theoretical modeling revealed a high bound biexciton ASE threshold beyond the damage threshold of PEPI, with no optical gain from free and bound excitons predicted. Several recommendations have also been proposed. A combination of these suggestions may be needed to overcome the optical gain challenge in 2D perovskites.

\textbf{ACKNOWLEDGEMENTS}

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is gratefully acknowledged.

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Figure 1 | Absence of ASE in PEPI. a, Schematic structure of PEPI, which consists of alternating organic $C_9H_3C_2H_4NH_3^+$ and inorganic $[PbI_6]^{4-}$ layers. The naturally formed quantum well structure enables the formation of tightly bound excitons with binding energy ($E_b$) $\sim$ 180 meV in the inorganic layers. b, Room temperature pump fluence dependent PL spectrum of PEPI. c, 10 K pump fluence dependent PL spectrum of PEPI showing three distinct emission peaks (Peak 1, 2 and 3). There is no superlinear increase in PL intensity for both temperatures. These optical experiments were conducted using 400 nm wavelength pump pulses (50 fs, 1 KHz).
Figure 2 | Low temperature bound exciton formation in PEPI. 

a, Temperature dependent PL spectrum of PEPI showing two distinct emission peaks (peak 1 and 2). b, Integrated PL intensity at different temperature for peak 1 and peak 2. The plot is fitted with a biexponential Arrhenius equation:

\[ I = \frac{I_0}{1 + A_1 \exp\left(-\frac{E_1}{k_BT}\right) + A_2 \exp\left(-\frac{E_2}{k_BT}\right)} \]

where \( I \) is the integrated PL intensity, \( I_0 \) is the integrated PL intensity at 0 K, \( A_1 \) and \( A_2 \) are the amplitudes, \( E_1 \) and \( E_2 \) are the activation energies, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. The larger energy (\( E_1 \)) is consistent with the exciton binding energy in PEPI. c, Integrated PL intensity at different temperature for peak 2. The small activation extracted with a single exponential Arrhenius equation is consistent with \( E_1 \) in b. d, Lifetime of peak 1 and 2 emission. These optical experiments were conducted using 400 nm wavelength pump pulses (50 fs, 1 KHz, 2.6 µJ/cm\(^2\) (steady-state PL) or 7.0 µJ/cm\(^2\) (time-resolved PL)).
Figure 3 | Rate equation analysis of energetics and kinetics from PEPI.  

a, Proposed schematics of the exciton (open circles) relaxation channels in PEPI. 

b, 10 K TRPL kinetics of peak 1 emission from PEPI. The kinetics is well modeled using a set of rate equations described in equation (1) to (6). Inset: 2D time-wavelength image of the PL emission with peak 1 labeled. The optical experiments were conducted using 400 nm wavelength pump pulses (50 fs, 1 KHz, 7 \( \mu \)J/cm\(^2\)). 

c, Integrated PL intensity of the deconvolved peaks as a function of laser intensity extracted from figure 1c. The points are well-fitted using the proposed rate equations. Inset: Integrated PL intensity modeled at higher laser fluence with predicted biexciton ASE threshold of 1.4 mJ/cm\(^2\).
**Figure 4 | Proposed strategies to promote optical gain** | **a,** Embedding 2D perovskite into a cavity (e.g. distributed Bragg reflector and distributed feedback cavity. Promoting single exciton gain using type II configuration by **b,** surrounding 2D perovskite nanocrystal with a suitable semiconductor shell or **c,** choosing an appropriate small bandgap organic constituent. **d,** Employing $(\text{H}_3\text{N}-\text{R}-\text{NH}_3)$PbI$_4$ structure to improve film morphology which in turn may reduce traps.
Table 1 | Description of the terms used in equation (1) to (6).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hbar \omega$</td>
<td>Pump photon energy.</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient at pump energy.</td>
</tr>
<tr>
<td>$\tau_{xr}$</td>
<td>Exciton radiative lifetime.</td>
</tr>
<tr>
<td>$k_{xnr}$</td>
<td>Exciton non-radiative relaxation rate.</td>
</tr>
<tr>
<td>$\tau_{xb}r$</td>
<td>Bound exciton non-radiative relaxation rate.</td>
</tr>
<tr>
<td>$k_{xbnr}$</td>
<td>Bound biexciton non-radiative relaxation rate.</td>
</tr>
<tr>
<td>$\tau_{xb}r$</td>
<td>Bound biexciton Radiative relaxation rate.</td>
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<tr>
<td>$\tau_{cx}$</td>
<td>Free carrier to exciton relaxation time</td>
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<tr>
<td>$\tau_{cxb}$</td>
<td>Free carrier to bound exciton relaxation time</td>
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<tr>
<td>$\tau_L$</td>
<td>Laser time constant</td>
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<tr>
<td>$C_X$</td>
<td>Bound exciton trapping</td>
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<tr>
<td>$B_{xxb}$</td>
<td>Bound biexciton formation coefficient</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Exciton-exciton annihilation coefficient</td>
</tr>
<tr>
<td>$v_{gx}$</td>
<td>Group velocity at exciton emission energy</td>
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<tr>
<td>$v_{gx_b}$</td>
<td>Group velocity at bound exciton emission energy</td>
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<tr>
<td>$v_{gxx_b}$</td>
<td>Group velocity at bound biexciton emission energy</td>
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</tbody>
</table>
Supplementary Information for:

Dominant Factors Limiting Optical Gain in Layered Two-Dimensional Halide Perovskite Thin Films†

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**Supplementary Figure S1** | **Disproportionate optical gain reports from 2D perovskite.** Pie chart depicting the number of optical gain reports from 2D\[^1\] and 3D perovskite\[^2\]–\[^28\]. Till date, there is only one claim of lasing from 2D perovskite cavity structure.
Supplementary Figure S2 | Characteristics of lasing phenomenon\textsuperscript{29}.  

\textbf{a,} Narrow emission linewidth with lasing wavelength dependent on cavity and gain medium. The gain bandwidth lies within the broad spontaneous emission region (condition 1 and 2).  

\textbf{b,} Threshold associated with integrated emission intensity and full width at half maximum (FWHM) (condition 3).  

\textbf{c,} Lasing output consists of a beam (condition 4).
X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Steady State absorption Characterization of PEPI. The XRD spectrum of the as-grown PEPI consists of periodic peaks with ~ 5° interval as shown in Fig. S3a. The periodic feature is representative of a layered structure and is typical for 2D perovskite\(^{30}\). The SEM image revealed good substrate coverage and sample morphology – Fig 3b. A strong excitonic absorption peak at 2.40 eV can also be observed - Fig. S3c. From the Tauc plot, the material bandgap and excitonic bandedge energy was estimated to be 2.42 eV and 2.24 eV respectively – Fig S3c inset. Taking the difference between these energy values, an exciton binding energy of ~180 meV can be obtained. This is consistent with several literatures\(^{31-33}\) and is typical for the excitonic 2D perovskite system.

Supplementary Figure S3 | Physical characterizations of PEPI. a, XRD spectrum of PEPI. Inset shows the magnified smaller periodic diffraction peaks. The broad peak center at 25° corresponds to the quartz substrate peak. b, SEM image of PEPI thin film showing good substrate coverage and sample morphology. c, Room temperature steady state absorption spectrum of PEPI. A sharp exciton absorption peak is observed at 516.5nm. Peaks at ~ 325 nm and ~ 400nm corresponds to transition from Pb 6s and I 5p hybridization orbital to Pb 6P orbital\(^{32}\). Inset shows the estimation of the exciton binding energy.
Supplementary Figure S4 | Effects of high laser fluence on low laser fluence PL spectrum.

Steady-state PL spectrum of PEPI excited with 400nm, taken at pump fluence of 1.3 µJ/cm², before and after exposure to high laser fluence of 177 µJ/cm². The damage threshold is defined here to be the laser fluence that reduces the PL intensity. Typical damage fluence found in PEPI is of the order of 100µJ/cm².
Supplementary Figure S5 | Effects of PMMA overlayer on PEPI PL emission. a, 10 K PL spectrum of PEPI with and without PMMA layer. Peak 2 is observed to quench significantly after PMMA deposition. b, 77 K PL spectrum of PEPI with and without PMMA layer. The degree of quenching from peak 2 was found vary among samples. This suggests that the origin of peak 2 could be related to both bulk and surface effect. c, Integrated PL intensity of PEPI with and without PMMA taken at 60 equally distributed sample spot across a ~ 0.75 x 0.75 cm² sample area. The average and standard distribution are also included. Time resolved PL spectrum of peak 1 with and without PMMA. There is a lifetime lengthening of peak 1 with PMMA is consistent with trap passivation. All experiments were conducted using 400 nm pulse excitation and laser fluence of 7 µJ/cm².
X-ray Photoelectron Spectroscopy (XPS) Studies. XPS study is employed to investigate the surface elemental composition of the perovskite since a large surface contribution has been found from peak 2. Supplementary Figure S6 (a) shows the XPS wide scan of PEPI film while figure (b), (c) and (d) shows the narrow scan of the respective C 1s, N 1s, Pb 4f and I 3d peaks. Supplementary Table S1 shows the surface elemental ratio of the perovskite obtained from the integrated area of the narrow scan. The results indicate that the surface contains organic vacancies, which could be responsible for peak 2 emission. The presence of small activation energy of 10 meV (see Figure 2) could arise from the energy barrier between the free exciton state and this vacancy state. Therefore, the occupancy of this vacancy state is likely due to transfer from free exciton state (peak 1).

Supplementary Figure S6 | XPS elemental peaks characterization of PEPI. a, XPS wide scan of PEPI with respective elements labeled. XPS narrow scan of the respective elemental peaks: (b) C 1S, (c) N 1S, (d) Pb 4f and (e) I 3d.
Supplementary Table S1 | Organic deficiency at PEPI surface. The surface elemental composition ratio is derived from the area under the respective XPS narrow scan curve in Figure S6 (b) to €. The element C and N were found to be lesser than the ideal case.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>N</th>
<th>Pb</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric Ratio</td>
<td>16</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>XPS Results</td>
<td>11.2</td>
<td>1.7</td>
<td>1.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>


Supplementary Figure S7 | Origins of peak 3. Plot of integrated PL intensity with pump fluence. The integrated PL intensity of the respective peaks is fitted with power law ($y_i = k_i x^{m_i}$). The exponent $m_i$ indicates the behavior of the respective species under different pump fluence. The value of $m_3$ for peak 3 is approximately twice compared to $m_1$ and $m_2$ for peak 1 and 2 respectively which suggests a biexcitonic origin. The reduction of $m_3$ to $m_4$ at higher laser fluence is likely due to exciton-biexciton scattering\textsuperscript{34}. The experiment were conducted using 400 nm pulse excitation of pristine PEPI thin film.
**PEPI biexciton binding energy determination.** The biexciton binding energy \( E_b \) is defined as

\[
E_b = 2E_x - E_{xx} = E_x - (E_{xx} - E_x)
\]

(S1)

where \( E_x \) is the exciton energy and \( E_{xx} \) is the biexciton energy. For PEPI, \( E_x \) corresponds to the bound exciton energy (peak 2). The radiative recombination of a biexciton involves a photon emission and an exciton formation. The photon emitted gives rise to the observed peak 3. Therefore, the biexciton binding energy is the energy difference between peak 3 and peak 2.
Supplementary Figure S8 | Significant quenching of biexciton emission. High laser fluence (~92 µJ/cm²) PL spectrum excited with and without PMMA overlayer. Peak 3 is observed to be quenched significantly after PMMA addition. The experiment was conducted using 400 nm pulse laser.
Supplementary Table S2. Parameters for the rate equations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Meaning</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hbar\omega$</td>
<td>Pump photon energy.</td>
<td>3.1 eV</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient at pump energy.</td>
<td>$2.086 \times 10^5$ cm$^{-1}$</td>
</tr>
<tr>
<td>$\tau_{xr}$</td>
<td>Exciton radiative lifetime.</td>
<td>100 ps</td>
</tr>
<tr>
<td>$k_{xnr}$</td>
<td>Exciton non-radiative relaxation rate.</td>
<td>0.011 ps$^{-1}$</td>
</tr>
<tr>
<td>$\tau_{xbr}$</td>
<td>Bound exciton non-radiative relaxation rate.</td>
<td>150 ps</td>
</tr>
<tr>
<td>$k_{xbnr}$</td>
<td>Bound biexciton non-radiative relaxation rate.</td>
<td>0.04 ps$^{-1}$</td>
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<tr>
<td>$\tau_{xxr}$</td>
<td>Bound biexciton Radiative relaxation rate.</td>
<td>50 ps</td>
</tr>
<tr>
<td>$D_X$</td>
<td>Density of states</td>
<td>$4 \times 10^{21}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$\tau_{cx}$</td>
<td>Free carrier to exciton relaxation time</td>
<td>50 fs</td>
</tr>
<tr>
<td>$\tau_{cXB}$</td>
<td>Free carrier to bound exciton relaxation time</td>
<td>10 fs</td>
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<tr>
<td>$\tau_L$</td>
<td>Laser time constant</td>
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<tr>
<td>$C_X$</td>
<td>Bound exciton trapping</td>
<td>9 ns$^{-1}$</td>
</tr>
<tr>
<td>$B_{XXB}$</td>
<td>Bound biexciton formation coefficient</td>
<td>$8 \times 10^{-21}$ cm$^3$</td>
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<tr>
<td>$\gamma$</td>
<td>Exciton-exciton annihilation coefficient</td>
<td>$3.38 \times 10^{-12}$ cm$^3$/s</td>
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<tr>
<td>$v_{gx}$</td>
<td>Group velocity at exciton emission energy</td>
<td>$1.14 \times 10^8$ m/s</td>
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<tr>
<td>$v_{gXB}$</td>
<td>Group velocity at bound exciton emission energy</td>
<td>$1.25 \times 10^8$ m/s</td>
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<tr>
<td>$v_{gXXB}$</td>
<td>Group velocity at bound biexciton emission energy</td>
<td>$1.31 \times 10^8$ m/s</td>
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<tr>
<td>$g_X$</td>
<td>Exciton optical gain</td>
<td>$1.038 \times 10^5$ cm$^{-1}$</td>
</tr>
<tr>
<td>$g_{XB}$</td>
<td>Bound exciton optical gain</td>
<td>$6.603 \times 10^4$ cm$^{-1}$</td>
</tr>
<tr>
<td>$g_{XXB}$</td>
<td>Bound biexciton optical gain</td>
<td>$4.964 \times 10^4$ cm$^{-1}$</td>
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</tbody>
</table>
References:


