**ESI**

*Substrate preparation*

The soda-lime glass substrates were cut into 1 cm × 1 cm. They were washed sequentially with dishwashing liquid, acetone, isopropanol and ethanol in ultrasonic bath and then treated under UV ozone for 30 min to remove residues.

*Perovskite film fabrication*

**MAPbI$_3$:** The perovskite solution with 1 M was prepared by dissolving a stoichiometric amount of methylammonium iodide (MAI, Dyesol) and lead iodide (PbI$_2$, 99%, Sigma Aldrich) in a mixture of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (7 : 3 vol/vol). The solution was spin-coated on to cleaned glass substrates at a speed of 4000 rpm with a ramp rate of 4000 rpm s$^{-1}$ for 60 s. Chlorobenzene was dropped onto the substrate 10 s before the end of the spin coating to speed up the crystallization process. The sample was then annealed at 100 °C for 10 min. All sample preparation was conducted in a glovebox with a nitrogen atmosphere.

**Cs$_{0.07}$Rb$_{0.03}$FA$_{0.765}$MA$_{0.135}$PbI$_{2.55}$Br$_{0.45}$:** The perovskite precursor solution contained 1.2 M lead iodide (PbI$_2$, 99%, Sigma Aldrich), 1.1 M formamidinium iodide (FAI, Dyesol), 0.2 M lead bromide (PbBr$_2$, 99.999%, Sigma Aldrich), 0.2 M methylammonium bromide (MABr, Dyesol), 0.091 M cesium iodide (CsI, 99.999%, Sigma Aldrich), and 0.039 M rubidium iodide (RbI, 99.9%, Sigma Aldrich) in 1 mL anhydrous DMF:DMSO (4:1, v/v, Sigma Aldrich). The solution was spin-coated on to cleaned glass substrates by two steps: first at a speed of 2000 rpm with a ramp rate of 200 rpm s$^{-1}$ for 10 s, and then at a speed of 4000 rpm with a ramp rate of 2000 rpm s$^{-1}$ for 20 s. Chlorobenzene was dropped onto the substrate 5 s prior to the end of the second step to speed up the crystallization process. The sample was then annealed at 100 °C for 45 min. All sample preparation was conducted in a glovebox with a nitrogen atmosphere.

*Calculation of generation rate*

The generation rate is calculated by the integral of generation at each depth divided by the thickness across the film:
\[ G = \frac{\int_{x=0}^{x=t} \alpha \varphi_0 e^{-\alpha x} \, dx}{t} = \frac{\varphi_0 (1 - e^{-\alpha t})}{t} \]

where \( \varphi_0 \) (cm\(^{-2}\)/s) is the photon flux at the surface; \( \alpha \) (cm\(^{-1}\)) is the absorption coefficient; \( x \) (cm) is the distance into the film; and \( t \) (cm) is the thickness of the film.

The photon flux is calculated from laser power, wavelength and spot size:

\[ \varphi_0 = \frac{I_0 \hbar c}{\lambda} \]
\[ I_0 = \frac{2P}{\pi w_0^2} \]

where \( I_0 \) (W/cm\(^2\)) is the laser intensity; \( \hbar \) (J \cdot s) is the Planck constant; \( c \) (cm/s) is the speed of light; \( \lambda \) (cm) is the wavelength of laser; \( P \) (W) is the laser power; and \( w_0 \) (cm) is the radius of the laser spot.

For example, in the measurement of steady-state PL intensity on MAPbI\(_3\) perovskite films, the wavelength of the laser used in this experiment is 532 nm, the absorption coefficient of MAPbI\(_3\) at this wavelength is \( 1.5 \times 10^4 \) cm\(^{-1}\), the measured laser power is 1 \( \mu \)W, the diameter of laser spot is shown in Figure S1 (a); and the thickness of the film is 200 nm. Then,

\[ I_0 = \frac{2P}{\pi w_0^2} = \frac{2 \times 10^{-6}}{\pi \times (3.6 \times 10^{-4}/2)^2} = 19.65 \text{ W/cm}^2 \]

\[ \varphi_0 = \frac{I_0 \hbar c}{\lambda} = 19.65 \times \frac{6.626 \times 10^{-34} \times 3 \times 10^{10}}{532 \times 10^{-7}} = 5.26 \times 10^{19} \text{ cm}^{-2}/\text{s} \]

\[ G = \frac{\varphi_0 (1 - e^{-\alpha t})}{t} = \frac{5.26 \times 10^{19} \times (1 - e^{-1.5 \times 10^4 \times 200 \times 10^{-7}})}{200 \times 10^{-7}} = 6.81 \times 10^{23} \text{ cm}^{-3}/\text{s} \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B ) (cm(^3)s(^{-1}))</td>
<td>( 1 \times 10^{-10} )</td>
</tr>
<tr>
<td>( N_t ) (cm(^{-3}))</td>
<td>( 1 \times 10^{16} )</td>
</tr>
<tr>
<td>( E_t ) (eV)</td>
<td>0.20</td>
</tr>
<tr>
<td>( \langle c_n \rangle ) (cm(^3)s(^{-1}))</td>
<td>( 1 \times 10^{-8} )</td>
</tr>
<tr>
<td>( \langle e_n \rangle ) (cm(^3)s(^{-1}))</td>
<td>( 5 \times 10^{-9} )</td>
</tr>
<tr>
<td>( \Gamma ) (cm(^6)s(^{-1}))</td>
<td>( 1 \times 10^{-31} )</td>
</tr>
<tr>
<td>( N_A ) (cm(^{-3}))</td>
<td>( 3 \times 10^{14} )</td>
</tr>
</tbody>
</table>

**Experiments**

Excitation-dependent steady-state PL measurement
Photoluminescence spectra measurements were performed using LabRAM HR Evolution System. A 532 nm DPSS-laser was used for excitation. The PL signal was extracted at 770 nm using a Syncerity CCD deep cooled camera. Both the incident light and the reflected light went through a 50x objective lens (LEICA PL FLUOTAR L 50×/0.55). The measured laser spot size is shown in Figure S1(a). The samples were kept in N₂ environment during the measurements. To change the excitation level, absorptive neutral density filters (AR-coated for 350-700 nm) – ND1, ND2, ND3, ND4 and ND5 were inserted in front of incident light. To protect the detector, absorptive neutral density filters (AR-coated for 650-1050 nm) – ND1, ND2, ND3, ND4 and ND5 were inserted in front of the detector.

Excitation-dependent transient PL measurement:

Time-resolved photoluminescence decay measurements were performed using LabRAM HR Evolution system with a time-correlated single photon counting (TCSPC) system (DeltaPro-DD, Horiba). A 508 nm diode laser (DD-510L, Horiba) with pulse duration of 110ps, fluence of ~10 μJ/cm²/pulse, and a repetition rate of 312.5kHz was used for excitation. The PL signal was extracted at 770 nm. Both the incident light and the reflected light went through a 50x objective lens (LEICA PL FLUOTAR L 50×/0.55). The measured laser spot size is shown in Figure S1(b). The samples were kept in N₂ environment during the measurements. To change the excitation level, neutral density filters (ND0.3 and ND0.6) were inserted in front of incident light.
Figure S1 The cross section plots of the Gaussian beam captured by CCD camera using LEICA PL FLUOTAR L 50x/0.55 objective lens for (a) 532 nm DPSS-laser and (b) 508 nm diode laser.

Figure S2 Normalized PL spectra extracted from MAPbI₃ film (red curve) and quadruple-cation film (blue curve).
Figure S3 Time-dependent PL intensity measured on a single spot over 600 s on (a) MAPbI$_3$ film and (b) quadruple-cation film at the maximum laser intensity. The measurements are taken on the area of the sample that had been measured (Point 1) and on a non-exposed area (Point 2).

Figure S4 shows a representative light current-voltage (JV) curve of standard CH$_3$NH$_3$PbI$_3$ perovskite cells fabricated at ANU with structure ITO/compact-TiO$_2$/mesoporous-TiO$_2$/CH$_3$NH$_3$PbI$_3$/Spiro-MeOTAD/Au. The details of the fabrication processes of this cell can be found in [1]. The inset shows the figures of merit of this cell.
Figure S4 Light IV curve of CH$_3$NH$_3$PbI$_3$ perovskite cell. The inset table shows the performance parameters of this cell.

Figure S5 shows a representative light J-V curve of standard Cs$_{0.07}$Rb$_{0.03}$FA$_{0.765}$MA$_{0.135}$PbI$_{2.55}$Br$_{0.45}$ perovskite cells fabricated at ANU with structure FTO/compact indium-doped TiO$_x$/mesoporous-TiO$_2$/PCBM:PMMA passivation layer/Cs$_{0.07}$Rb$_{0.03}$FA$_{0.765}$MA$_{0.135}$PbI$_{2.55}$Br$_{0.45}$/Spiro-MeOTAD/Au. The details of the fabrication processes of this cell can be found in [2]. The figures of merit of this cell are shown in the inset.

The calculation of NRMSE

For excitation-dependent PL peak intensity,

\[
NRMSE_{PL} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \log_{10}(P_{model}) - \log_{10}(P_{exp}) \right)^2}
\]

For time-resolved PL decay at each of the excitation level,
\[
NRMSE_{\text{Decay}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \log_{10}(\text{Decay}_{\text{model}}) - \log_{10}(\text{Decay}_{\text{exp}}) \right)^2}
\]

Then, the combined NRMSE is calculated by taking the average of \(NRMSE_{PL}\) and the average of three \(NRMSE_{\text{Decay}}\) values for each sample.

\[
NRMSE = \frac{1}{2} \left( NRMSE_{PL} + \frac{1}{n} \sum_{i=1}^{n} NRMSE_{\text{Decay}} \right)
\]

To improve the accuracy of the fitting, the logarithm of the data was taken since the measured PL intensities in both experiments are varied by several orders of magnitude.

References
