Supplementary Information

Fabrication

Quartz glass substrates were used for the preparation of all films in this work. Before deposition, the quartz substrates were ultrasonically cleaned in isopropanol for 15 min, rinsed thoroughly with deionized water, and dried with high-purity nitrogen gas to remove residual solvent and moisture from the surface.

$CsPbI_3$ thin films were prepared by physical vapor deposition using an LN-386SA multi-source thermal evaporation system. The deposition was carried out under a high-vacuum condition of approximately 2×10^{-4} Pa. CsI and PbI_2 were used as the inorganic precursors, while benzohydrazide (BH) and $ZnBr_2$ were introduced as the organic molecule and metal-halide dopants, respectively. The evaporation rates of all sources were monitored in real time using quartz crystal microbalances to ensure accurate control of the film composition.

For BH-doped $CsPbI_3$ films, BH was introduced during the deposition of CsI and PbI_2. The nominal precursor thicknesses were CsI (100 nm), PbI_2 (100 nm), and BH (20, 30, or 40 nm). The BH weight fraction was calculated according to the following equation:

$$wt\%_{BH} = \frac{T_{BH}\cdot\rho_{BH}}{(T_{CsI}\cdot\rho_{CsI})+(T_{PbI_2}\cdot\rho_{PbI_2})+(T_{BH}\cdot\rho_{BH})}\times 100\%\#(S1)$$

where T and ρ represent the nominal thickness and density of the corresponding component, respectively. The calculated BH weight fractions were 2.2, 3.3, and 4.3 wt%, and the corresponding samples were denoted as BH-2.2, BH-3.3, and BH-4.3, respectively. Based on the optimization of the BH-doped films, the BH content was fixed at 3.3 wt% for the subsequent BH/$ZnBr_2$ co-doped samples.

For the BH/$ZnBr_2$ co-doped $CsPbI_3$ films, CsI, PbI_2, BH, and $ZnBr_2$ were co-evaporated onto quartz glass substrates. The BH content was maintained at 3.3 wt% for all co-doped samples. During deposition, the evaporation rate of PbI_2 was fixed at 0.7 Å s^{-1}, while the evaporation rates of $ZnBr_2$ were set to 0.10, 0.15, and 0.20 Å s^{-1}. To compensate for the compositional variation introduced by $ZnBr_2$ and maintain the perovskite precursor ratio, the evaporation rates of CsI were adjusted to 0.80, 0.85, and 0.90 Å s^{-1}, respectively. The total film thickness was controlled within approximately 200–300 nm.

The Zn/(Pb + Zn) molar percentage was estimated from the evaporation parameters according to:

$$n \propto \frac{R\cdot\rho}{M}\#(S2)$$

where R, ρ, and M represent the evaporation rate, density, and molar mass of the corresponding precursor, respectively. The calculated Zn/(Pb+Zn) molar percentages were 16.6, 23.0, and 28.5 mol%. Therefore, the co-doped films were denoted as BH-Zn-16.6, BH-Zn-23.0, and BH-Zn-28.5, respectively.

After deposition, the as-prepared doped films were immediately transferred onto a preheated hot plate and annealed at 70 °C for 5 min in air (20°C, 60%RH). The thermal annealing process promoted the conversion of the initially formed yellow δ-phase into the black photoactive perovskite phase. The pristine $CsPbI_3$ and BH-only doped films were prepared under comparable deposition conditions and used as reference samples. Due to their limited phase stability during temperature cycling, reliable temperature-dependent recombination parameters could not be obtained for these reference films; therefore, only their room-temperature recombination parameters were used for comparison.

Time-resolved PL (TRPL) – Excitation Intensity

The TRPL measurements were performed using a 300 nm pulsed laser with a repetition rate of 1 MHz. The excitation fluence was calculated according to:

$$F = \frac{P_{Avg}}{f\cdot A}\#(S3)$$

where F is the excitation fluence, P_{Avg} is the average laser power, (f) is the repetition rate, and (A) is the laser spot area. In the TRPL measurements, the laser spot area was approximately 1.0×10^{-5} cm^2, corresponding to a circular spot diameter of about 36 μm. Under low excitation conditions, the average laser power was 0.4 μW, giving an excitation fluence of approximately 40 nJ cm^{-2}. Under high excitation conditions, the average laser power was increased to 40 μW, corresponding to an excitation fluence of approximately 4.0 μJ cm^{-2}.

Fitting of Temperature Dependent PL-Exciton Binding Energy (E_B)

To quantitatively evaluate the exciton stability, temperature-dependent photoluminescence (TDPL) measurements were performed to determine the exciton binding energy (E_B). The exciton binding energy was obtained by fitting the integrated PL intensity using the Arrhenius model described by Eq. (1) in the main text.

By applying a non-linear least squares fitting to the experimental data, the value of E_B was derived. This fitting procedure allows for the characterization of the competition between radiative recombination and thermal dissociation of excitons into free carriers, providing insights into the optoelectronic quality of the modified films.

Fitting of Room Temperature TRPL-τ_{Avg}

To characterize the charge-carrier dynamics at room temperature, the time-resolved photoluminescence (TRPL) decay curves were fitted using the bi-exponential decay model described in Eq. (3) in the main text. In this model, A_i and τ_i represent the pre-exponential factor and decay lifetime of the (i)-th component, respectively. Generally, the fast decay component (τ_1) is associated with trap-assisted non-radiative recombination at film surfaces and grain boundaries, whereas the slow decay component (τ_2) is mainly related to radiative recombination in the bulk perovskite region.

To quantitatively compare the overall carrier lifetime among different samples, the intensity-weighted average lifetime (τ_{Avg}) was calculated using the following equation:

$$\tau_{avg} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \#(S4)$$

The obtained τ_{Avg} values were used as an indicator of the overall carrier recombination behavior and the effectiveness of defect passivation in the perovskite films.

Fitting of FWHM of temperature dependent PL- Γ_0, Γ_{LO}, $\hbar\omega_{LO}$

To investigate the influence of exciton–phonon interactions on the optical properties of the films, the temperature-dependent full width at half maximum (FWHM) of the PL spectra was quantitatively analyzed. The experimentally obtained FWHM values in wavelength units (nm) were first converted into energy units (meV). The converted linewidth values from 77 K to 298 K were then fitted using the Bose–Einstein model described in Eq. (2) in the main text.

The fitting was performed using a non-linear least-squares method in Origin. The extracted parameters include the temperature-independent inhomogeneous broadening (Γ_0), the exciton–longitudinal optical phonon coupling strength (Γ_{LO}), and the LO phonon energy ($\hbar\omega_{LO}$). Here, Γ_0 reflects static disorder, defect-related broadening, and grain-boundary scattering, while Γ_{LO} describes the strength of exciton–LO phonon coupling and thermally induced dynamic scattering. During the fitting process, $\hbar\omega_{LO}$ was constrained within a physically reasonable range according to reported values for halide perovskites to ensure stable convergence and physically meaningful fitting results.

k_1 - Derived from temperature dependent TRPL

To quantitatively evaluate trap-assisted non-radiative recombination, the monomolecular recombination rate constant $k_1$was extracted from time-resolved photoluminescence (TRPL) measurements. All measurements were performed under a low excitation intensity to ensure that carrier dynamics were dominated by the monomolecular regime, in which higher-order processes such as bimolecular radiative recombination and Auger recombination can be neglected.

The TRPL decay curves were fitted using a bi-exponential function, as described in Eq. (3) in the main text, via a non-linear least-squares fitting procedure. The intensity-weighted average lifetime (τ_{Avg}) was then calculated according to Eq. (S4) in the Supplementary Information. In this regime, the monomolecular recombination rate constant was defined as the inverse of the average lifetime, i.e., $k_1 = 1/\tau_{Avg}$.

This extraction procedure was systematically applied over the temperature range from 77 K to 298 K, enabling analysis of the temperature dependence of k_1 and the evaluation of defect-related activation processes.

The carrier recombination dynamics in three-dimensional perovskites are generally described by the rate equation given in Eq. (4) in the main text.

Energy level determination from XPS and UV–Vis spectroscopy

The electronic energy levels of the $CsPbI_3$ thin films were determined by combining X-ray photoelectron spectroscopy (XPS) and UV–Vis absorption measurements. The valence band maximum (VBM) was extracted from the XPS valence band spectra by linear extrapolation of the leading edge to the baseline. The optical bandgap (E_g) was obtained from the Tauc plot by fitting the linear region of $(\alpha h\nu)^2$ versus photon energy (hν) and extrapolating to the energy axis intercept.

The conduction band minimum (CBM) was then calculated using the following relationship:

$$E_{CBM} = -E_{VBM} + E_g \#(S5)$$

This procedure allows for the determination of the energy band structure and band alignment of the $CsPbI_3$ thin films.