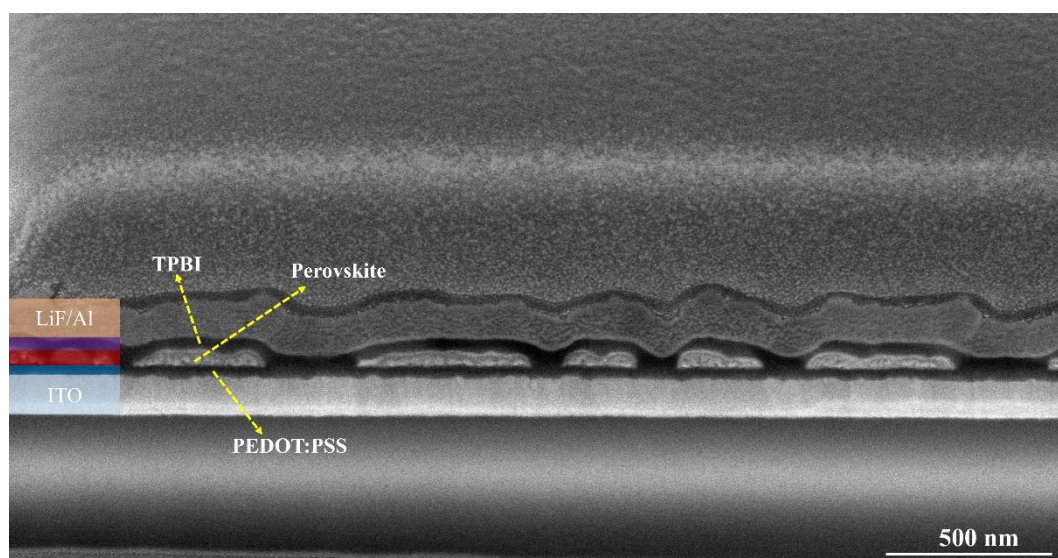


Bright and stable near-infrared lead-free perovskite light-emitting diodes

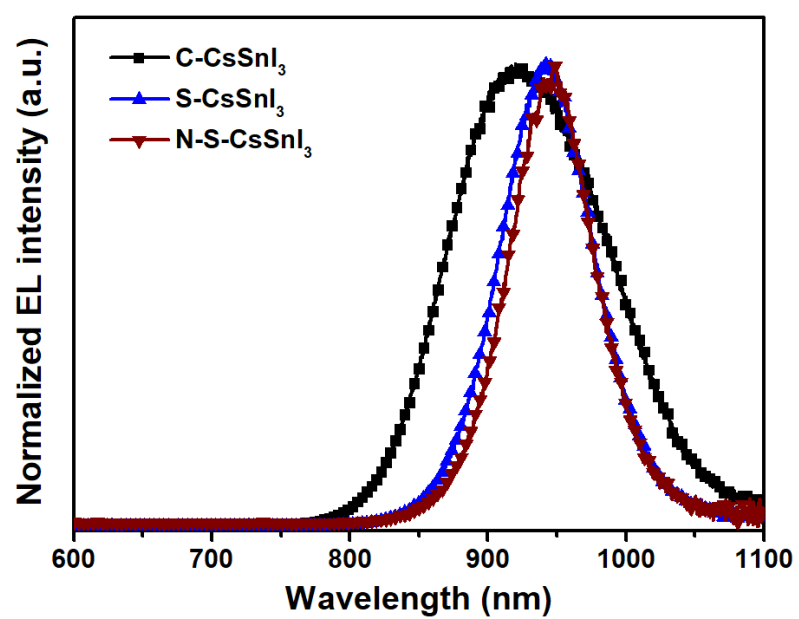
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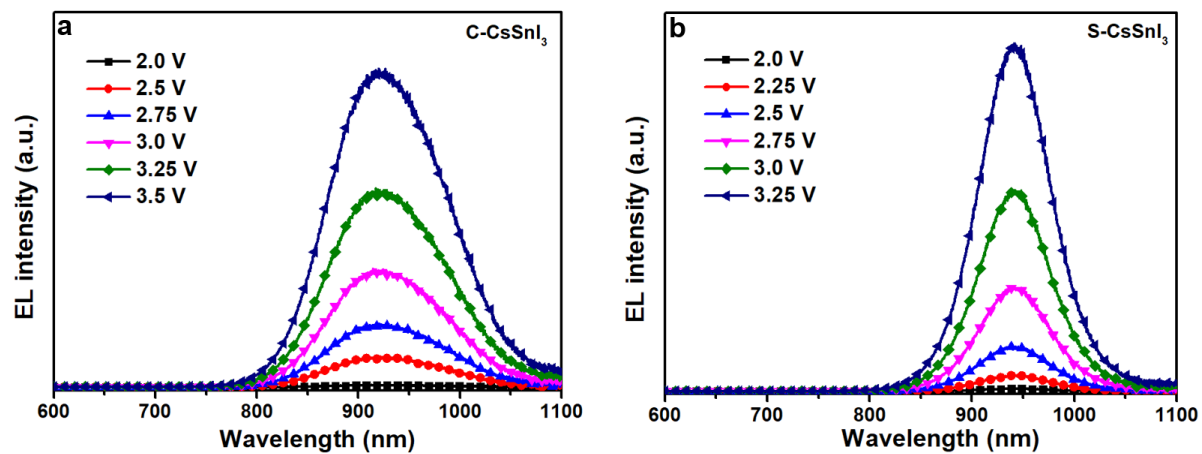
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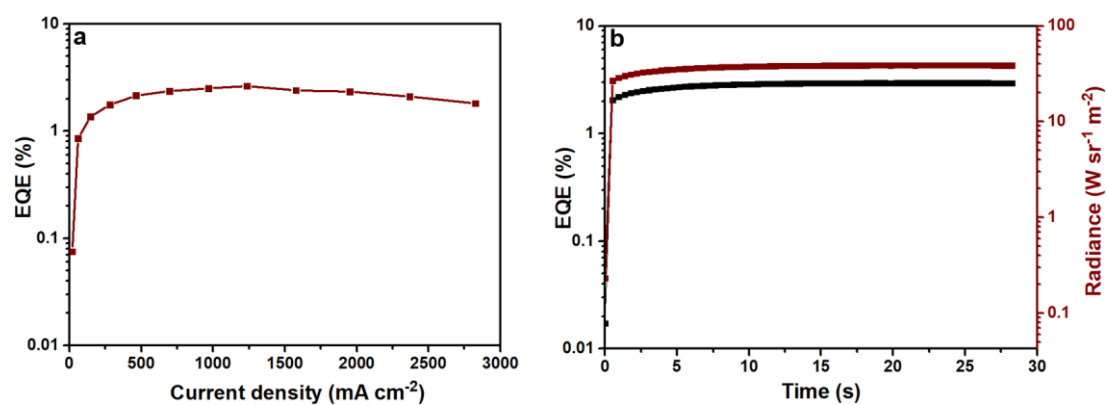
Supplementary Figure 1. Cross-sectional SEM image of the device.



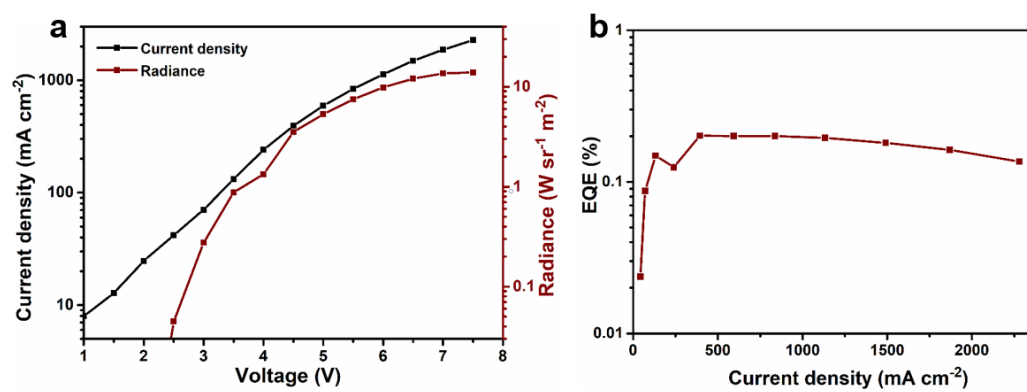
Supplementary Figure 2. Normalized EL spectra of LEDs based on CsSnI₃ prepared under different conditions.



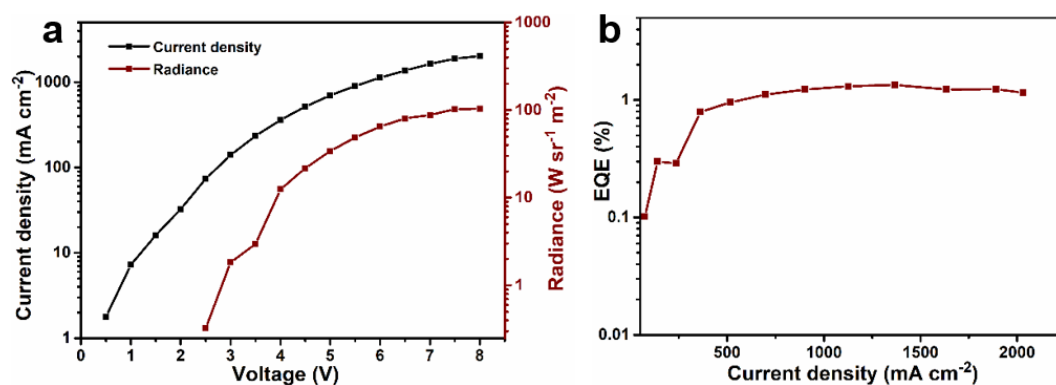
Supplementary Figure 3. EL spectra of C-CsSnI₃ (a) and S- CsSnI₃ (b) LEDs operated at different operation voltages.



Supplementary Figure 4. (a) EQE-current density characteristics. (b) The steady-state output radiance and EQE of the N-S-CsSnI₃ LEDs operated under a high current density of 300 mA cm⁻².

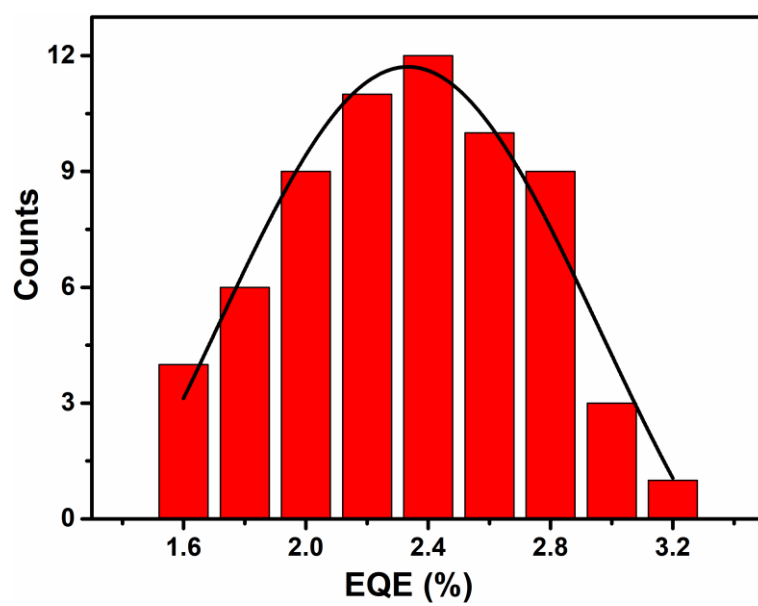


Supplementary Figure 5. Current density-voltage-radiance (a) and (b) EQE-current density characteristics of C-CsSnI₃ LEDs.

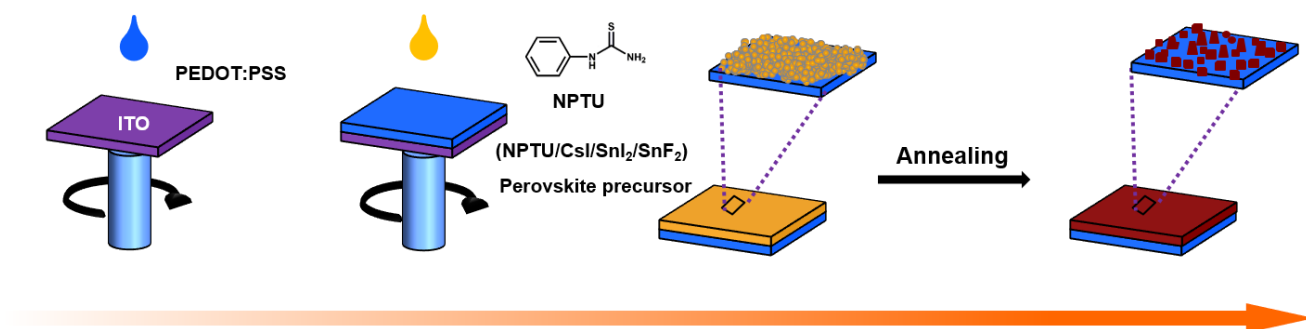


Supplementary Figure 6. Current density-voltage-radiance (a) and (b) EQE-current density characteristics of S-CsSnI₃ LEDs.

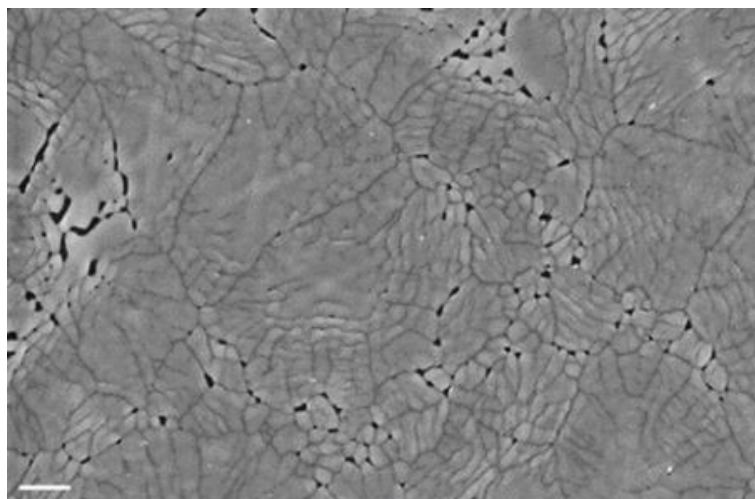
The Sn-based NIR LEDs have commonly exhibited a turn-on voltage higher than that of the bandgap, possibly due to the high background hole doping concentration and trap densities. The intrinsic high hole doping concentrations and trap densities will increase carrier collisions and nonradiative recombination. Therefore, a higher voltage is required to drive carriers through the emission layer and generate light emission.



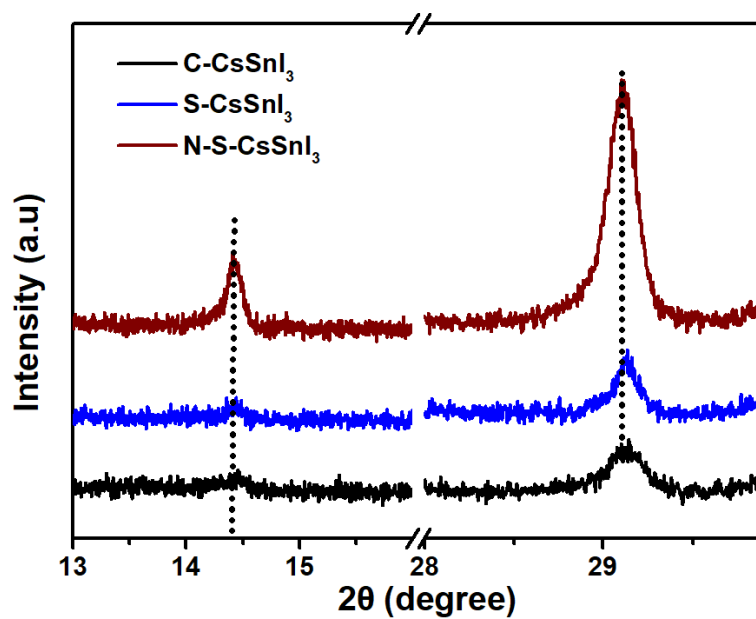
Supplementary Figure 7. The histograms of peak EQEs of N-S-CsSnI₃ LEDs.



Supplementary Figure 8. Schematic illustration of the preparation of the CsSnI₃ emissive layer of devices.

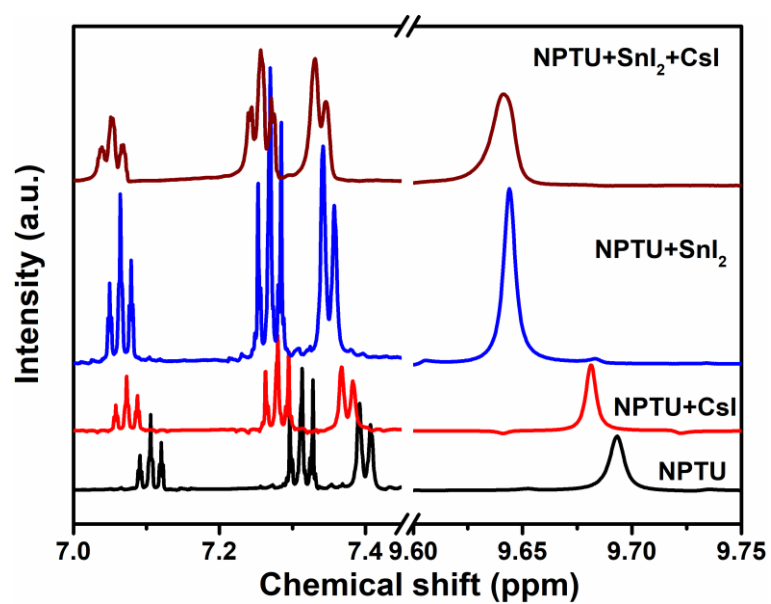


Supplementary Figure 9. SEM image of the CsSnI₃ film prepared without additives spin-coated on PEDOT:PSS. The scale bar is 1 μm .

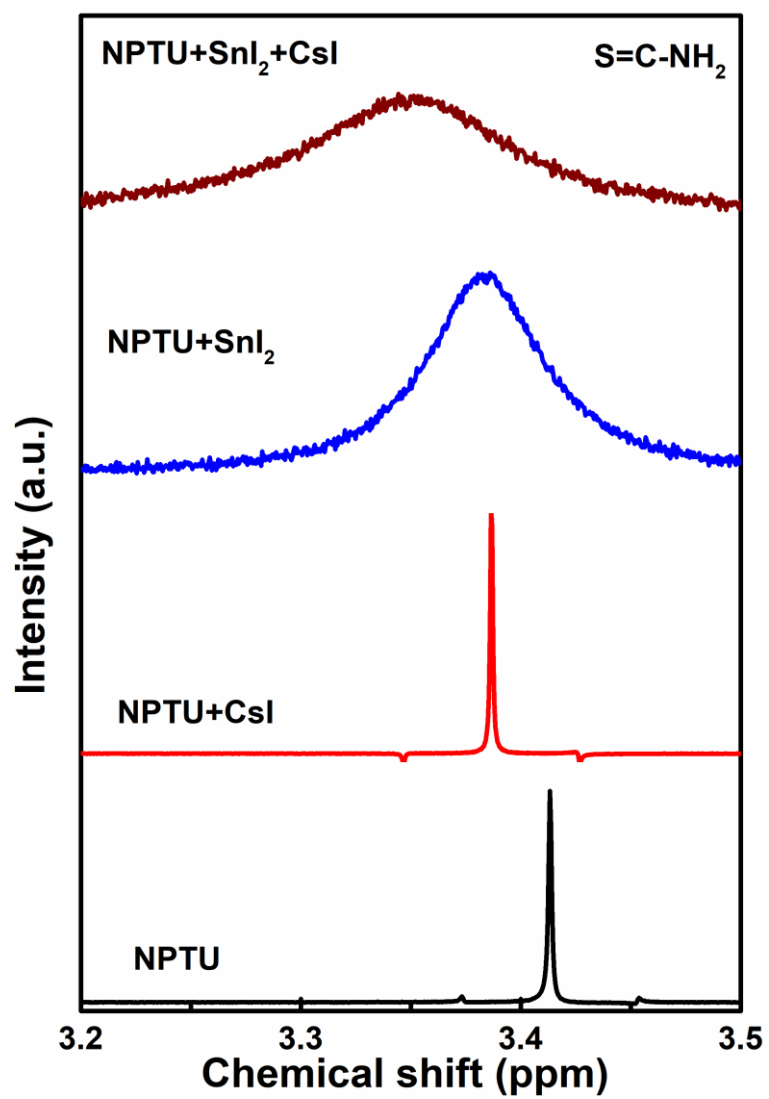


Supplementary Figure 10. XRD spectra of CsSnI₃ films prepared under different conditions.

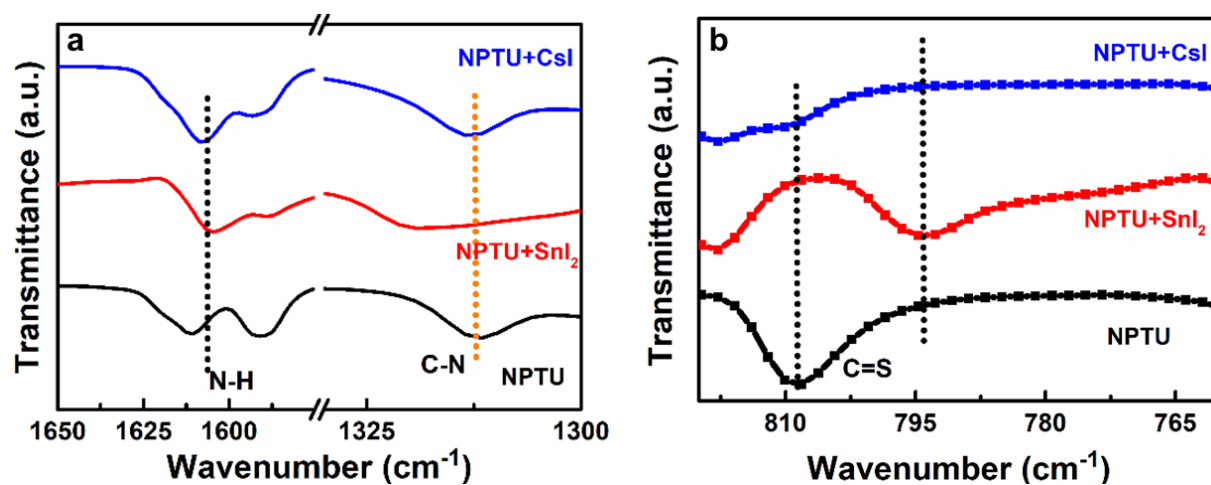
The negligible shift ($< 0.05^\circ$) observed in the (202) peak of the N-S-CsSnI₃ sample, as compared to the C- and S-CsSnI₃ samples, suggests that the NPTU has not been incorporated into the crystal lattice.



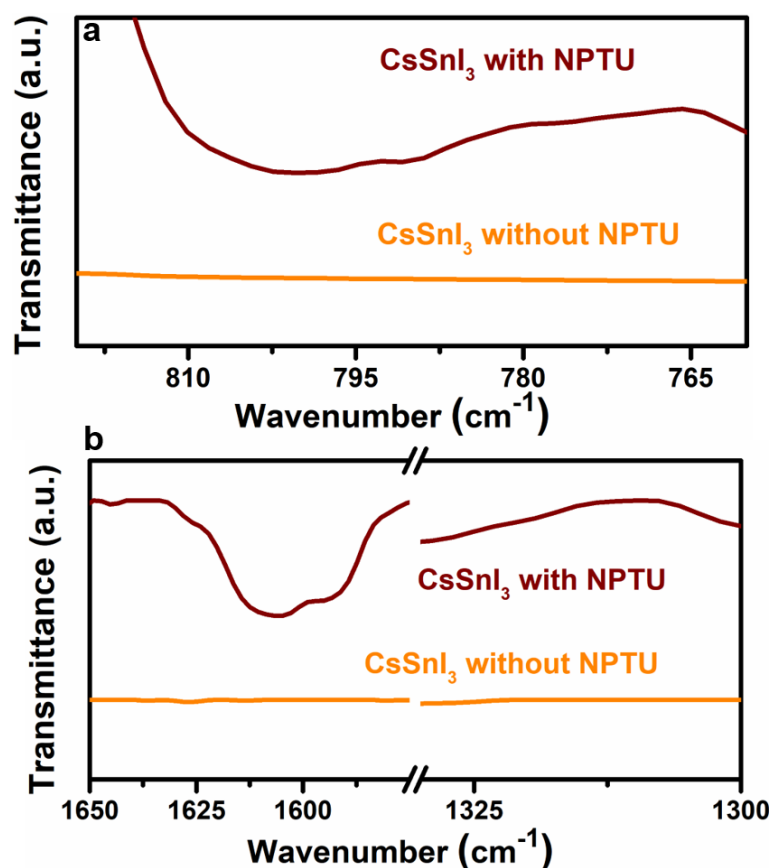
Supplementary Figure 11. ^1H NMR spectra of NPTU, NPTU+CsI, NPTU+SnI₂ and NPTU+CsI+SnI₂ in DMSO-d₆ solution.



Supplementary Figure 12. ^1H NMR spectra of NPTU, NPTU+CsI, NPTU+SnI₂ and NPTU+CsI+SnI₂ in DMSO-d₆ solution.



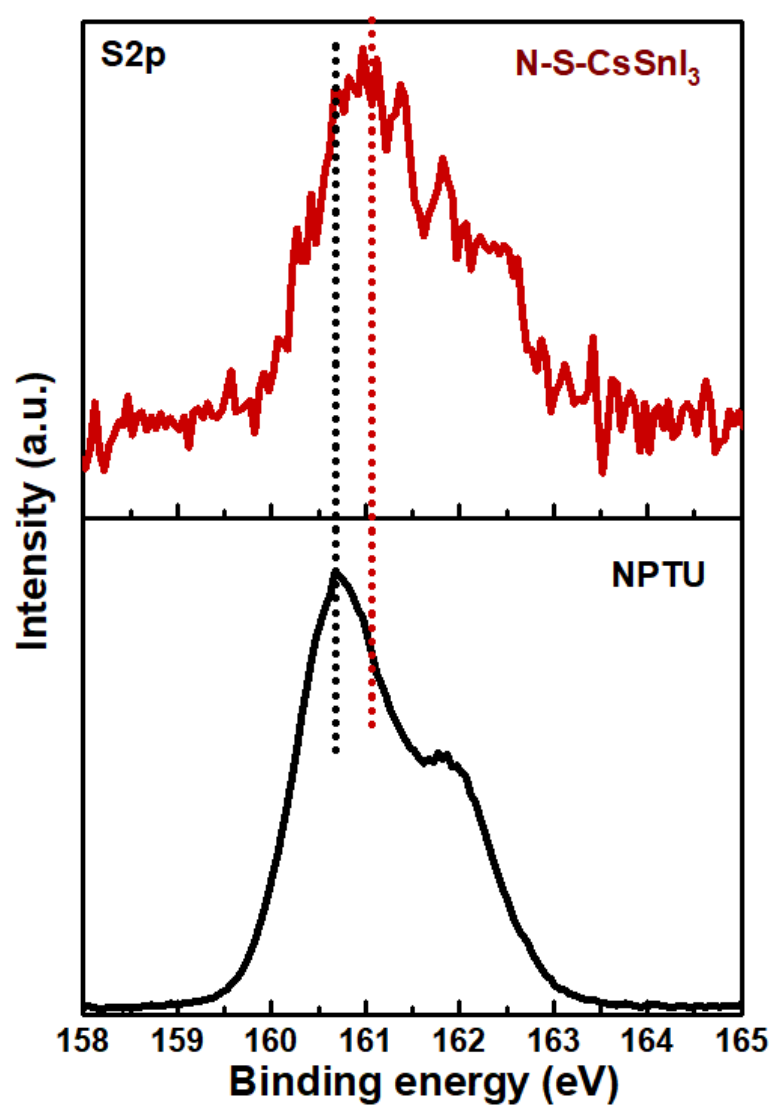
Supplementary Figure 13. ATR-FTIR spectra of NPTU, NPTU+CsI and NPTU+SnI₂.



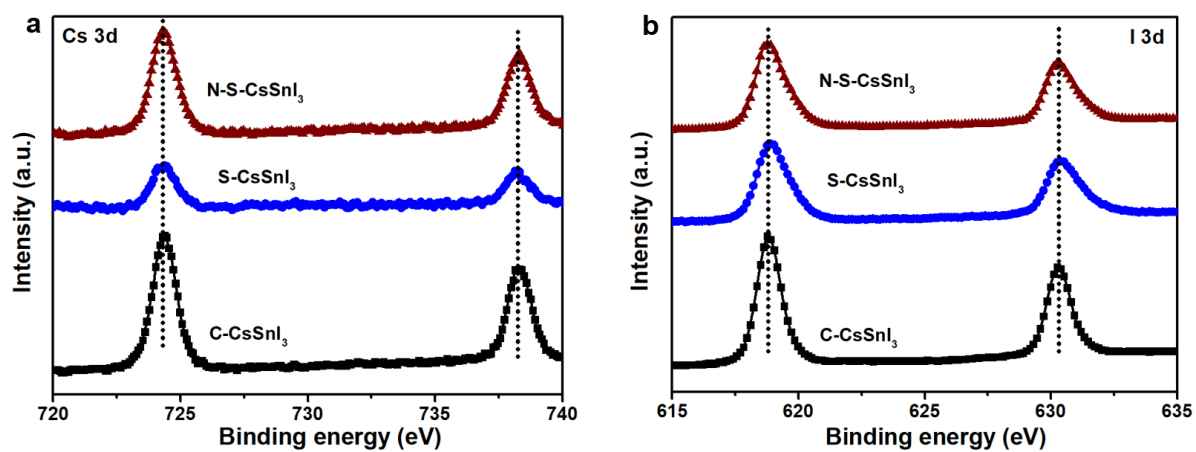
Supplementary Figure 14. ATR-FTIR spectra of CsSnI₃ films prepared with and without NPTU.

The stronger interaction between NPTU and SnI₂ has also been further confirmed by the ¹H NMR spectroscopy of NPTU, showing a larger chemical shift of N-H after interacting with SnI₂ compared with that of interacting with CsI (Supplementary **Fig. 11, 12**). ATR-FTIR spectroscopy further confirms the Lewis acid-base interaction mechanism between NPTU and the perovskite. The N-H bending vibration shifts from 1612 cm⁻¹ to lower wavenumber at 1608 cm⁻¹ and 1605 cm⁻¹ after interacting with CsI and SnI₂/CsSnI₃, respectively (Supplementary **Fig. 13, 14**). This small shift of N-H bending vibration band could be ascribed to the formation of weak hydrogen bonding between the N-H group in NPTU and I⁻, which has also been further confirmed by the small shift of C-N stretching vibration band at 1311 cm⁻¹ for NPTU and 1313 cm⁻¹ for NPTU+CsI. However, the C-N stretching vibration band of NPTU shifts to 1320 cm⁻¹ after interacting with SnI₂, which could result from the strong Lewis acid-base interaction of N-C=S⁺···Sn²⁺. The C=S stretching vibration band shifts from 808 cm⁻¹ to lower wavenumber at 793 and 797 cm⁻¹ after interacting with SnI₂ and CsSnI₃, revealing the strong interaction between Sn²⁺ and NPTU in the

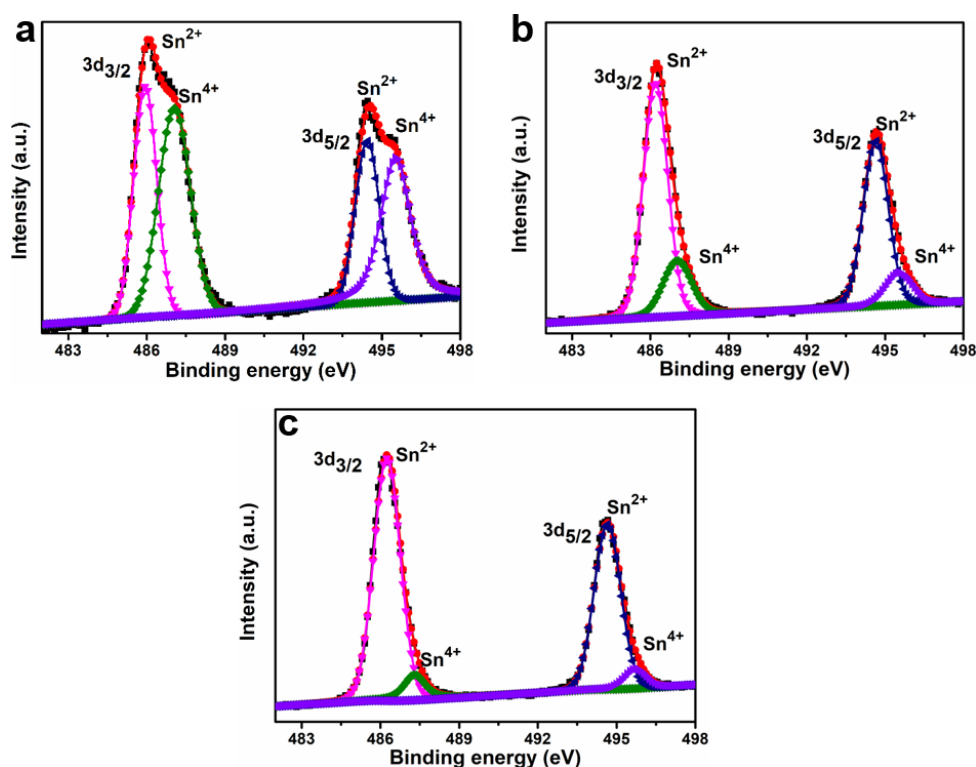
coordination bonding form of $\text{N-C=S}\cdots\text{Sn}^{2+}$. The shift of the stretching vibration band of C=S is caused by the delocalization of the lone electron pairs of the sulfur to the 5p empty orbitals of Sn^{2+} ($4\text{d}^{10}5\text{s}^2$). In addition, almost no obvious shift of the C=S stretching vibration band of NPTU could be observed after addition of CsI, which confirms that there is almost no obvious interaction between N-C=S and I^- . The above detailed NMR and FTIR spectroscopy provides evidence of the coordination of NPTU with Sn ions, leading to the formation of the controllable homogeneous grains.



Supplementary Figure 15. High-resolution S 2p XPS spectra of NPTU and N-S-CsSnI₃ films.

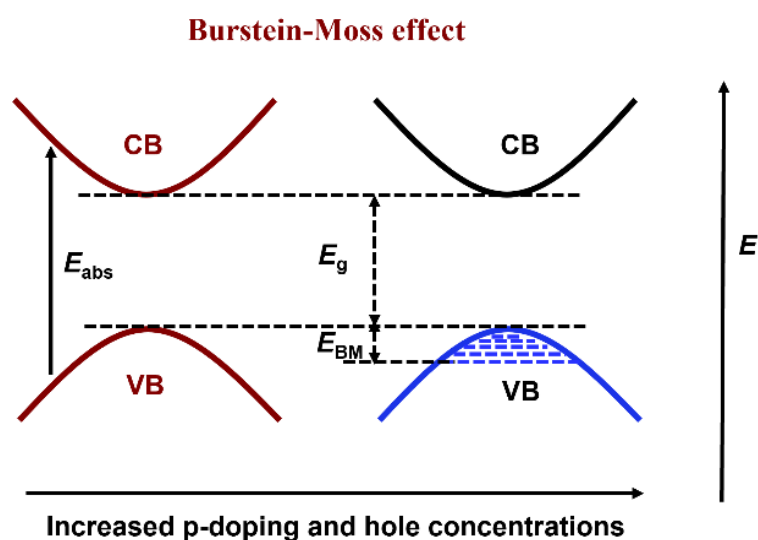


Supplementary Figure 16. The high-resolution Cs 3d (a) and I 3d (b) XPS spectra of CsSnI₃ films prepared under different conditions.



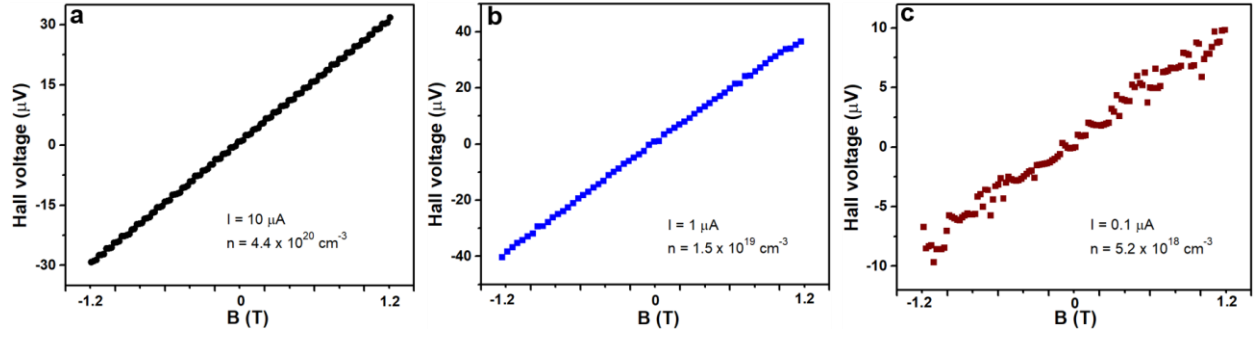
Supplementary Figure 17. The high-resolution Sn 3d XPS spectra of C-CsSnI₃ films (a), S-CsSnI₃ films (b) and N-S-CsSnI₃ films (c).

By combining NMR, FTIR and XPS results, we conclude that the N-C=S functional groups in NPTU form strong Lewis acid-base coordination bonding with Sn²⁺ in the form of N-C=S $\cdots$ Sn²⁺. The interaction could consequently retard the perovskite nucleation, control crystallization process, leading to improved crystallinity. The NPTU molecules at surfaces and grain boundaries of perovskite crystals lead to efficient surface passivation with reduced deep level trap state density originating from undercoordinated Sn²⁺ ion and Sn²⁺ oxidation. In addition, these NPTU molecules could also possibly prevent water and oxygen molecules from penetrating into the perovskite lattices, and thus may contribute to improved structural stability of CsSnI₃ films and corresponding operational stability of LED devices.

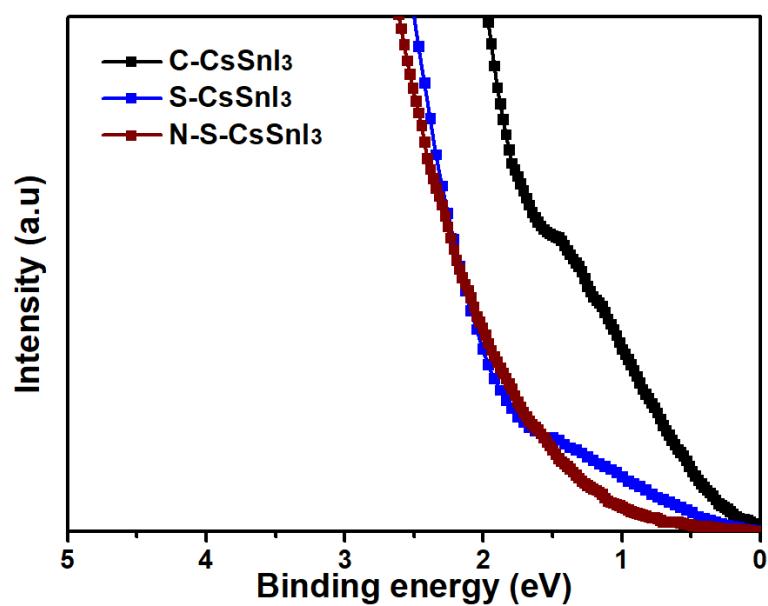


Supplementary Figure 18. Schematic representation of the Burstein-Moss effect which results in the enlarged optical bandgap due to the increased p-doping and hole concentrations of perovskite films.

With strong hole doping, the Fermi level shifts towards the valence band. As the Fermi level moves closer to the energy levels involved in electronic transitions, it affects the population of these energy levels. The increased population of states near the valence band edge results in a higher probability of radiative recombination, leading to emission at higher energies and a blueshift of the emission spectra. Strong hole doping can enhance scattering processes, such as carrier-carrier scattering and carrier-phonon scattering. These scattering events lead to energy exchange between the carriers and lattice vibrations, resulting in a broadening of the emission spectra.

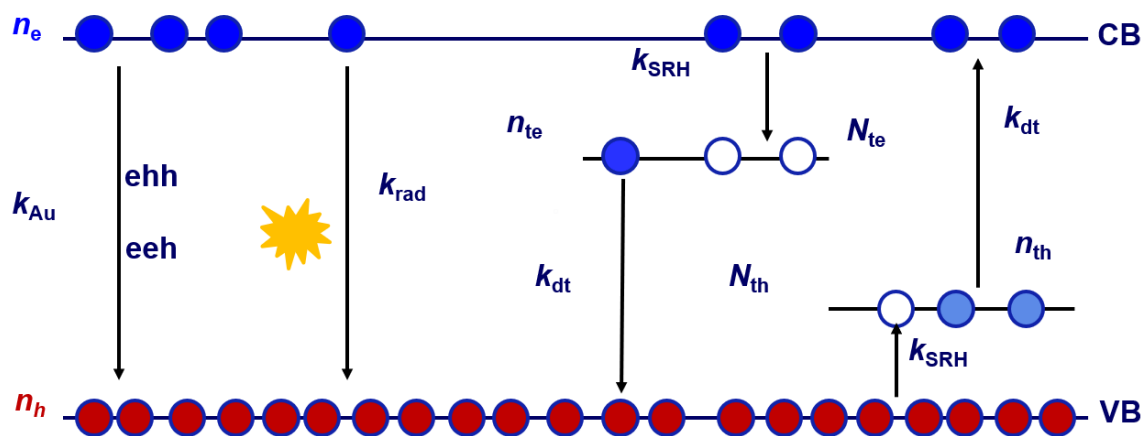


Supplementary Figure 19. Hall voltage vs magnetic field H in C- (a), S- (b) and N-S-CsSnI₃ films (c).

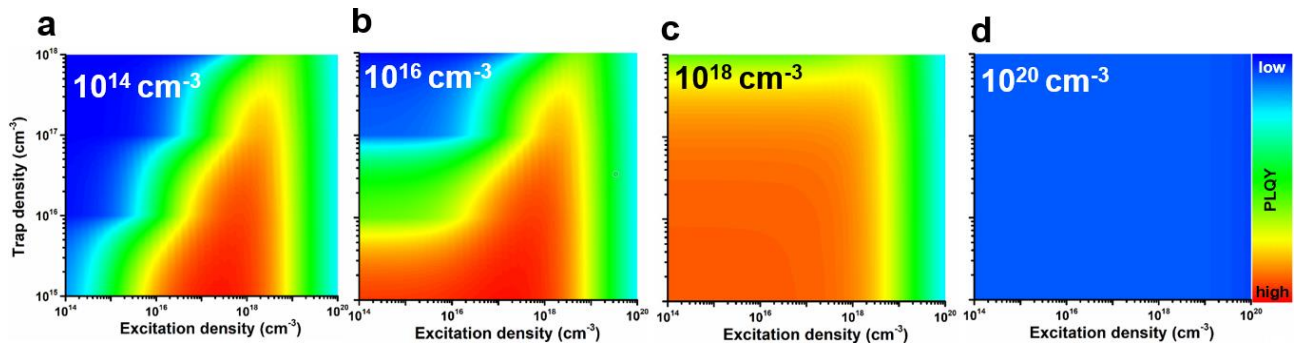


Supplementary Figure 20. UPS spectra of C-, S- and N-S-CsSnI₃ films.

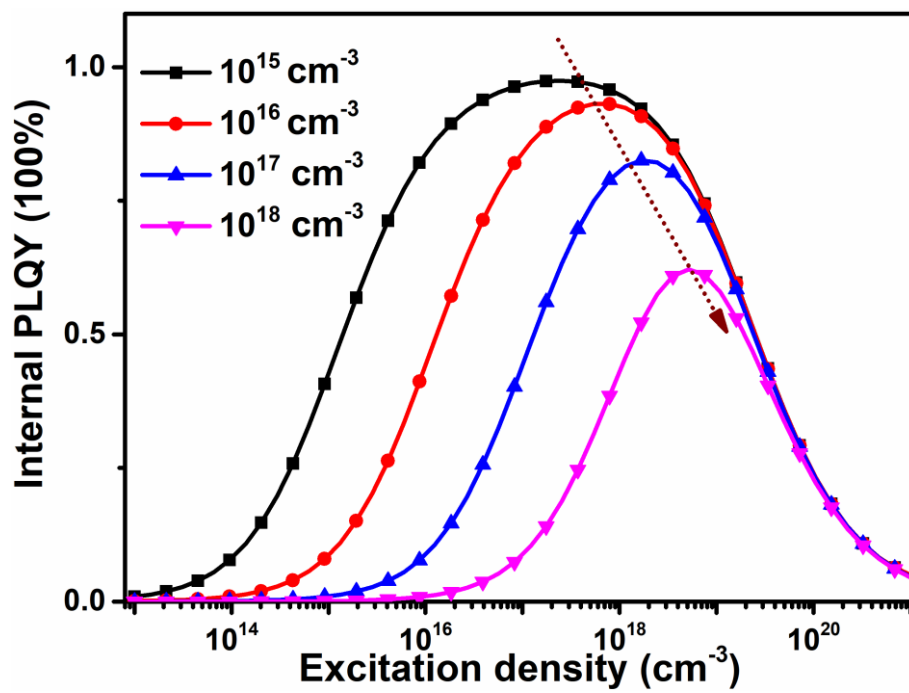
The change of the Fermi level induced by the hole doping concentration has also been confirmed by UPS spectra, which demonstrate a gradual shift of the Fermi level towards the valence band, from N-S-CsSnI₃ to S-CsSnI₃ and further to C-CsSnI₃ (Supplementary **Fig. 20**). This observation suggests that the hole doping concentration in C-CsSnI₃ is greater than that in S-CsSnI₃, while N-S-CsSnI₃ exhibits the lowest hole doping concentration.



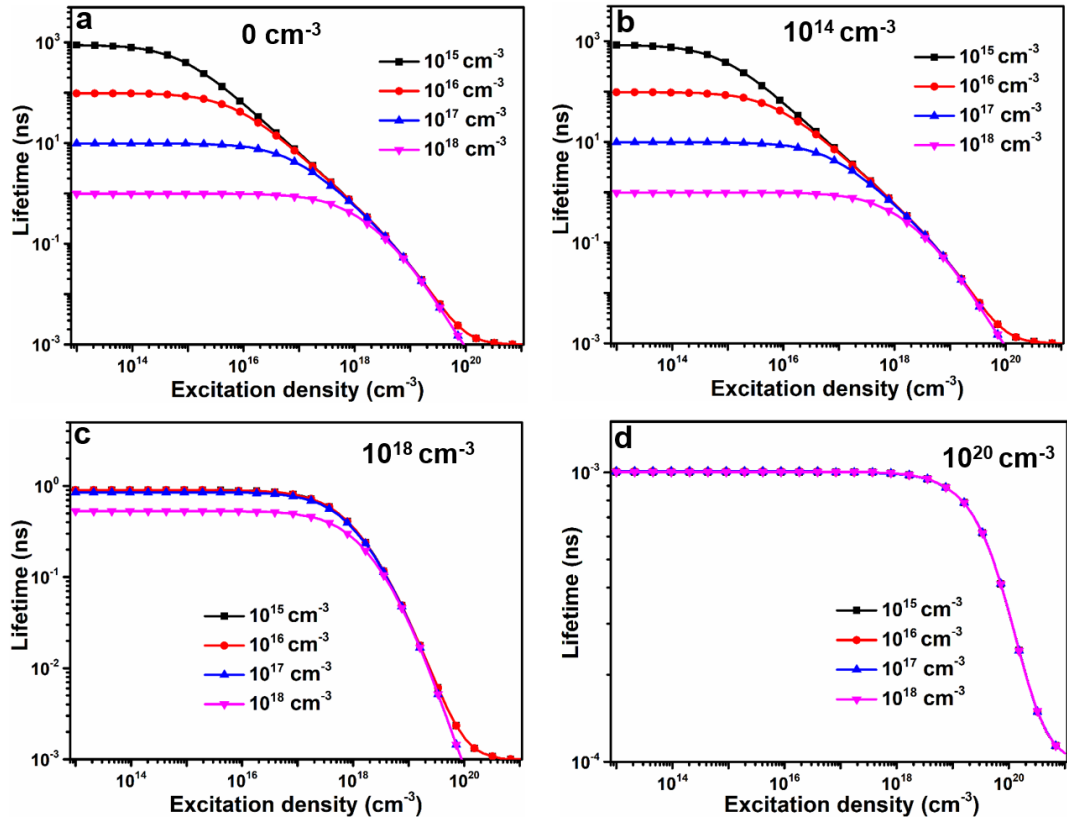
Supplementary Figure 21. Schematic illustration of the carrier recombination dynamic processes.



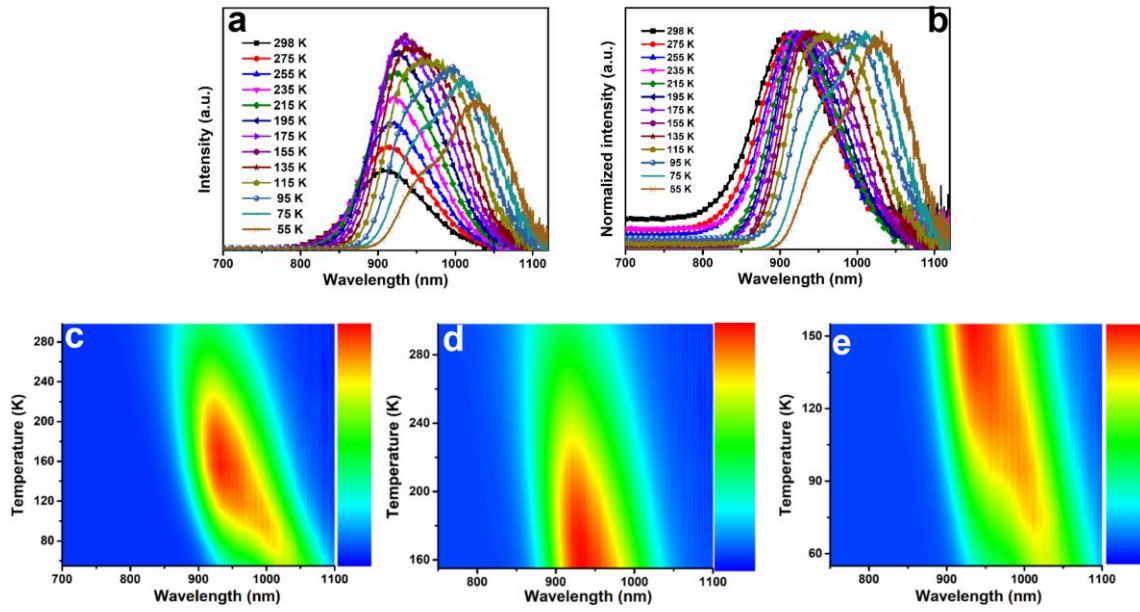
Supplementary Figure 22. Simulated excitation density-dependent internal PLQY of CsSnI₃ with different trap densities (10^{15} to 10^{18} cm⁻³) and different p-doping densities of (a) 10^{14} , (b) 10^{16} , and (c) 10^{18} (d) 10^{20} cm⁻³.



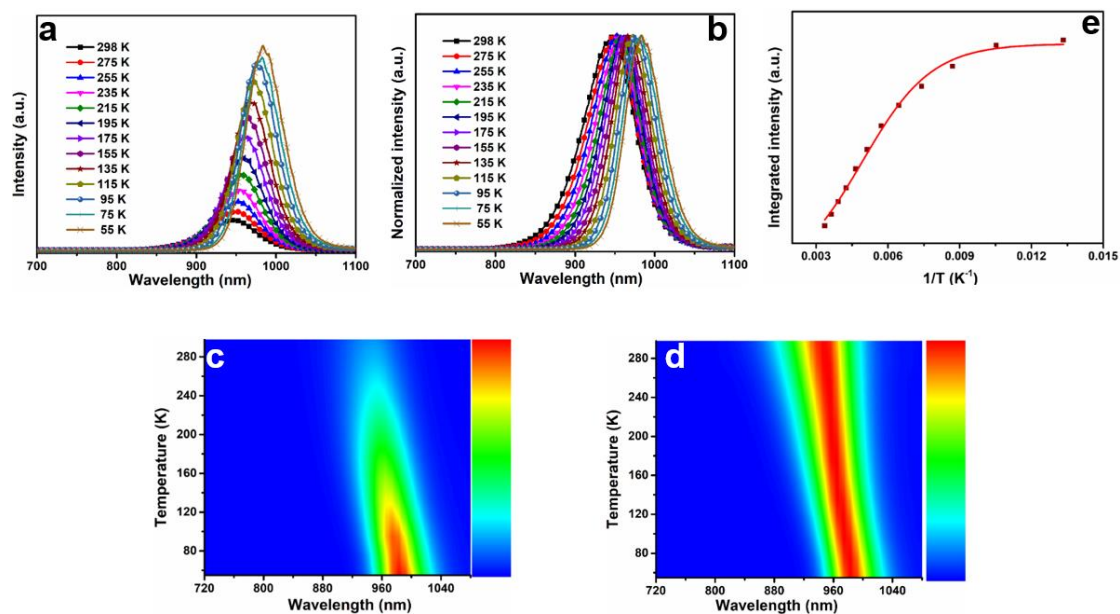
Supplementary Figure 23. Simulated excitation density-dependent internal PLQY of CsSnI₃ with different trap densities from 10¹⁵ to 10¹⁸ cm⁻³ and without hole doping density.



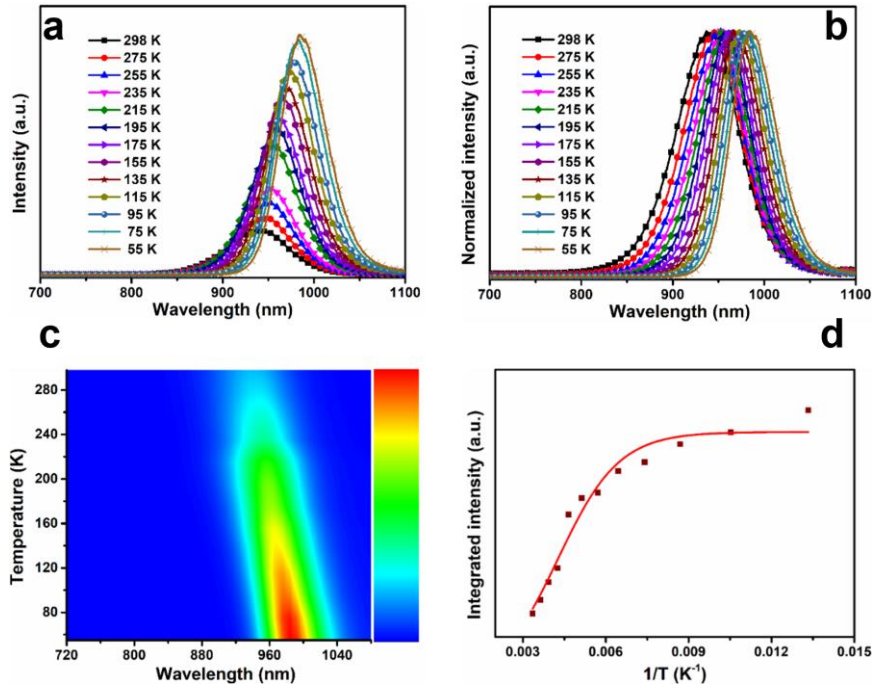
Supplementary Figure 24. Simulated excitation density-dependent carrier lifetime of CsSnI₃ with different trap densities from 10^{15} to 10^{18} cm⁻³ and hole doping densities of (a) 0, (b) 10^{14} , (c) 10^{18} and (d) 10^{20} cm⁻³.



Supplementary Figure 25. Low temperature-dependent PL spectra of C-CsSnI₃ film. PL spectra (a) and normalized PL spectra (b) from 55 to 298 K. Pseudocolor map of low temperature-dependent PL spectra from 55 to 298 K (c), 155 to 298 K (d) and 55-155 K (e).



Supplementary Figure 26. Low temperature-dependent PL spectra of S-CsSnI₃ films. PL spectra (a) and normalized PL spectra (b) from 55 to 298 K. Pseudocolor map of low temperature-dependent PL spectra (c) and normalized PL spectra (d). (e) Integrated PL emission intensity as a function of temperature.

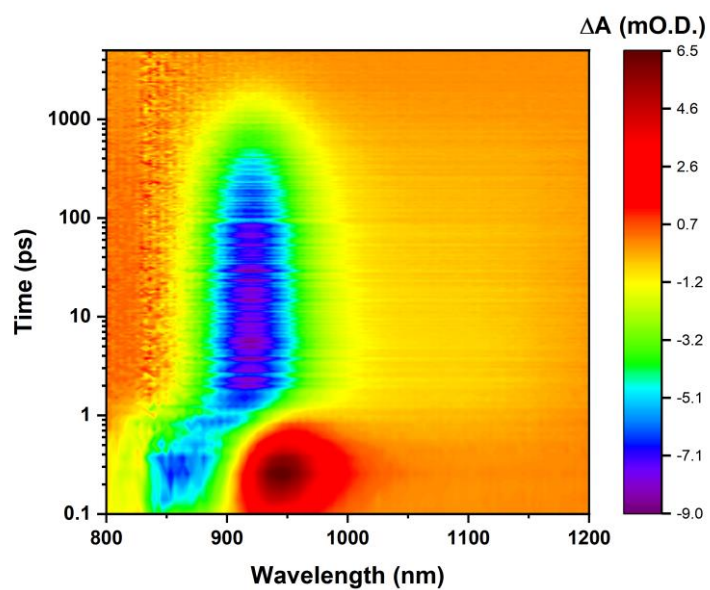


Supplementary Figure 27. Low temperature-dependent PL spectra of N-S-CsSnI₃ films. PL spectra (a) and normalized PL spectra (b) from 55 to 298 K. (c) Pseudocolor map of low temperature-dependent PL spectra. (d) Integrated PL emission intensity as a function of temperature.

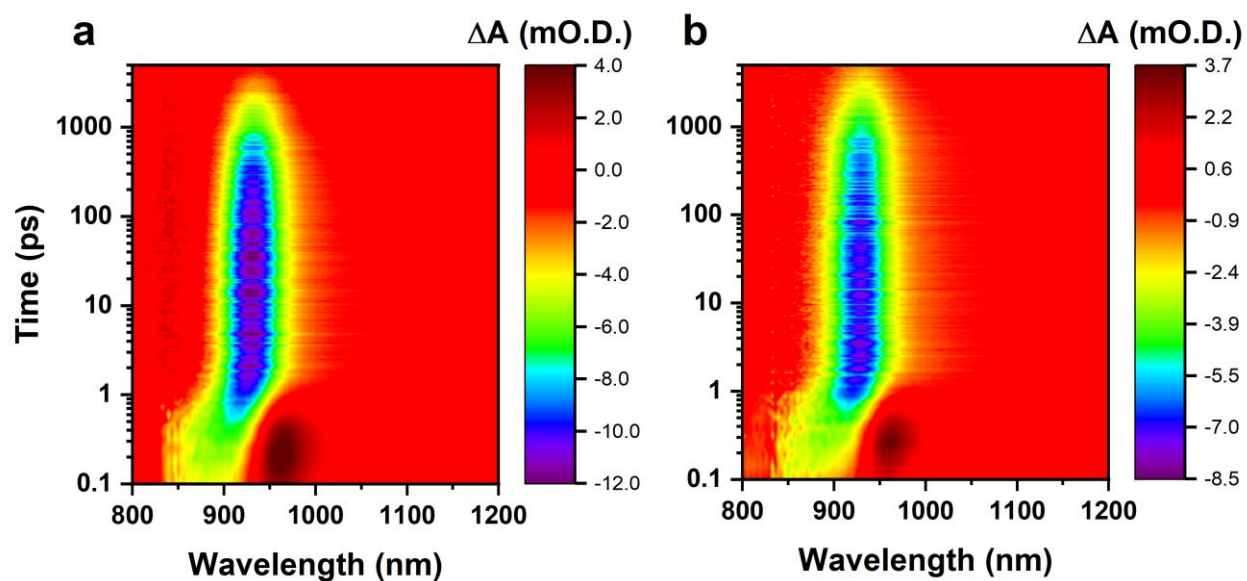
The low temperature-dependent PL and femtosecond transient absorption (fs-TA) spectra are measured to obtain a deeper insight into the presence of deep trap states in CsSnI₃. The C-CsSnI₃ show a red-shifted emission peak from 915 to 957 nm with decreasing temperature from 298 to 115 K (Supplementary Fig. 25), while a dominated emission peak centered above 1000 nm appears when the temperature decreases from 115 to 55 K. The newly emerging emission peak in the longer wavelength probably arises from the deep level trap states whose radiative recombination is activated at low temperatures. In contrast, the S- and N-S-CsSnI₃ show a continuously red-shifted emission peak and narrowing PL spectra with decreasing temperature from 298 to 55 K (Supplementary Fig. 26, 27). To extract the activation energy, the integrated PL emission intensity as a function of inverse temperature can be fitted by an Arrhenius plot with one effective thermal activation process, where I_0 is the integrated emission intensity at 0 K, k_B is the Boltzmann constant and E_{ac} denotes the activation energy for the non-radiative recombination processes. The effective activation energies are fitted to be 59 and 78 meV for the S- and N-S-CsSnI₃ films, respectively (Supplementary Fig. 26, 27). For the C-CsSnI₃ films, the PL intensity increases with decreasing temperature

from 298 to 155 K, and then decreases with decreasing temperature from 155 to 55 K (Supplementary **Fig. 25**). The temperature-dependent PL spectra cannot be fitted using the Arrhenius equation, which could possibly be caused by the extremely high trap density in the control films.

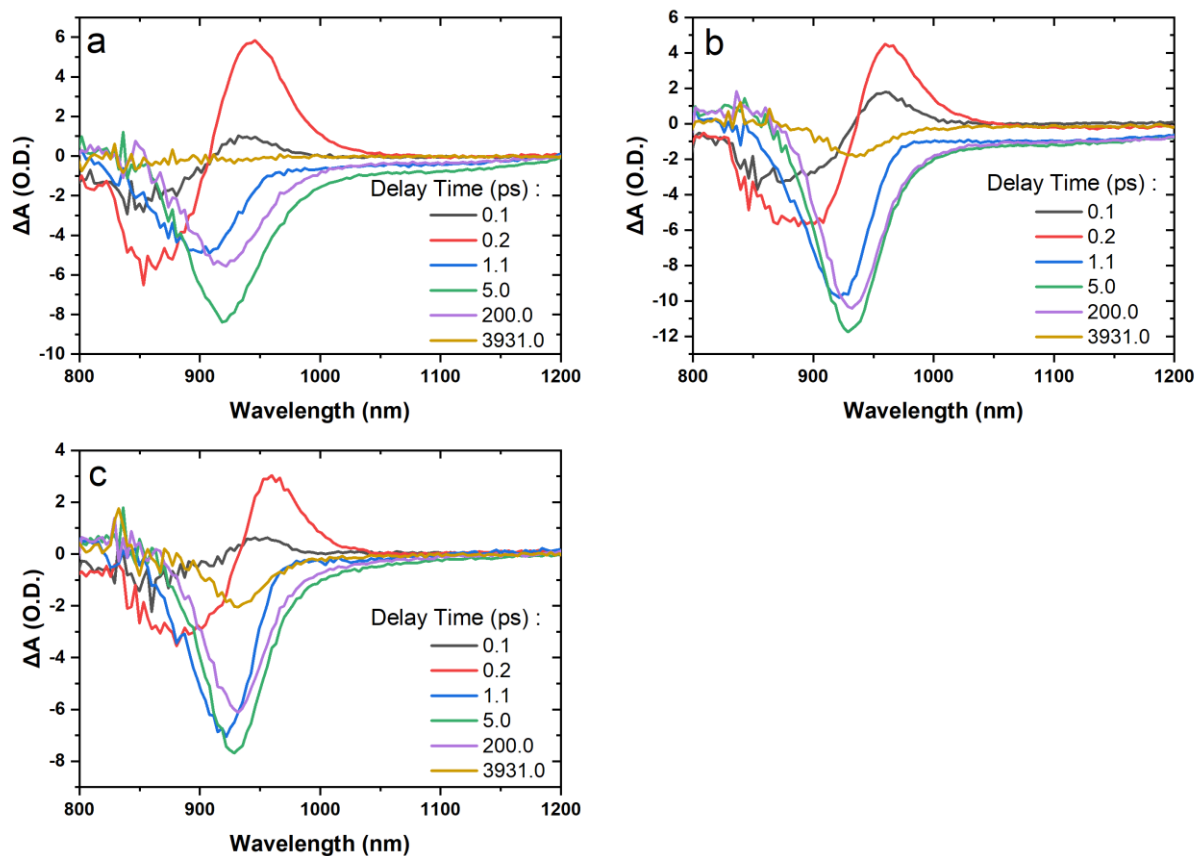
$$I(T) = \frac{I_0}{1 + Ae^{\frac{-E_{ac}}{k_B T}}}$$



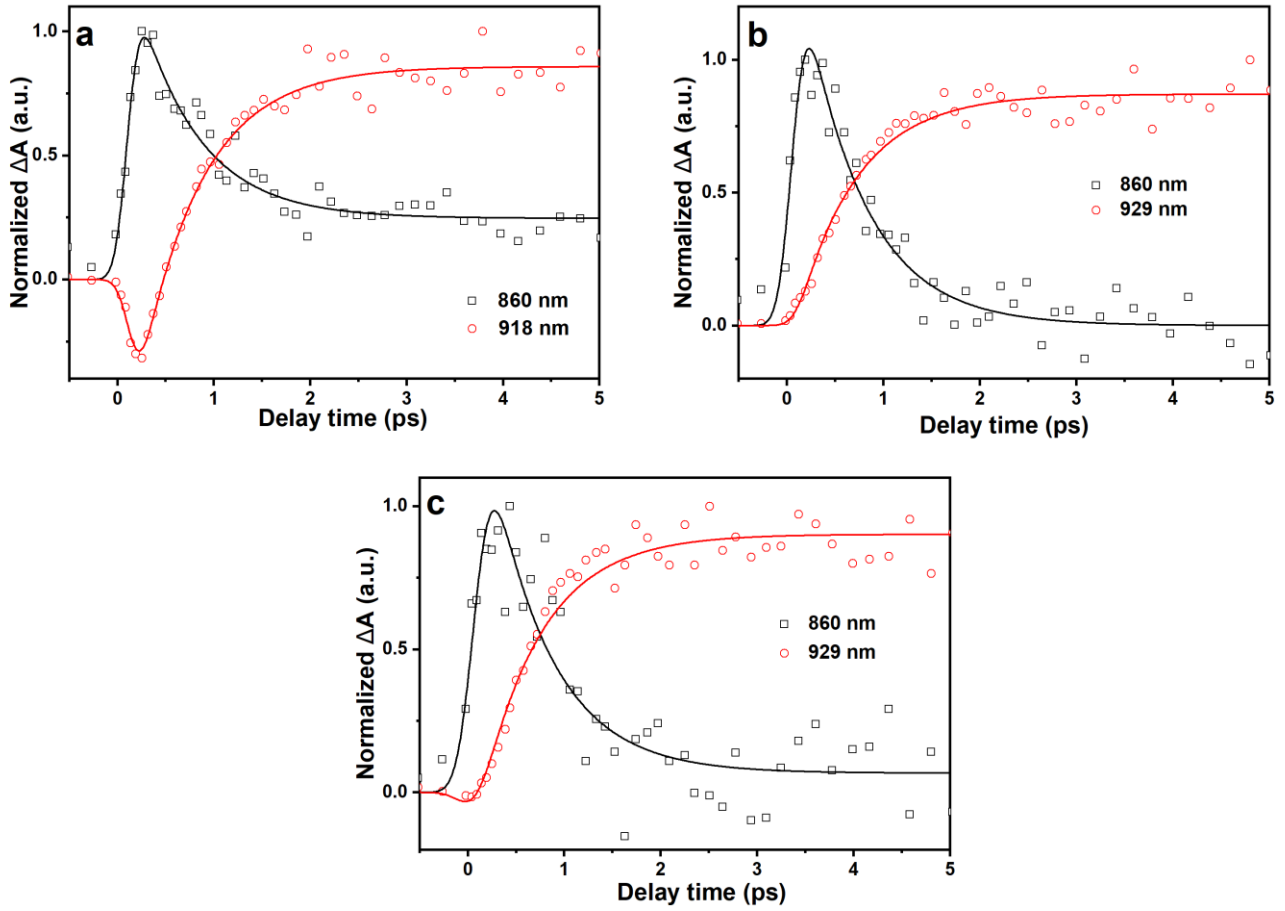
Supplementary Figure 28. Pseudocolor map of fs-TA spectra of C-CsSnI₃ films expressed as ΔA (the change of the absorption intensity of the sample after excitation at 650 nm with pump fluence of 1.6 $\mu\text{J}/\text{cm}^2$) as a function of both delay time and probe wavelength.



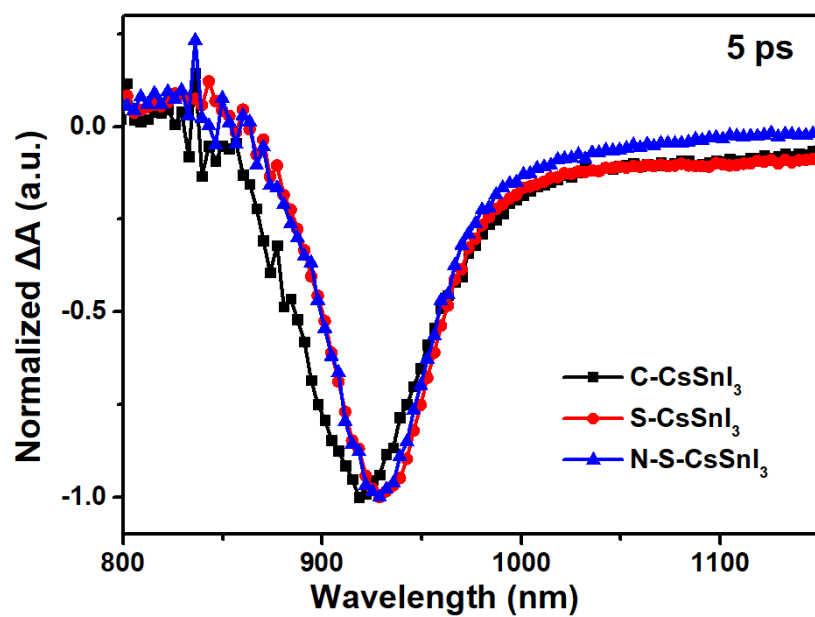
Supplementary Figure 29. Pseudocolor map of fs-TA spectra of S- (a) and N-S-CsSnI₃ (b) films expressed as ΔA (the change of the absorption intensity of the sample after excitation at 650 nm with pump fluence of 1.6 $\mu\text{J}/\text{cm}^2$) as a function of both delay time and probe wavelength.



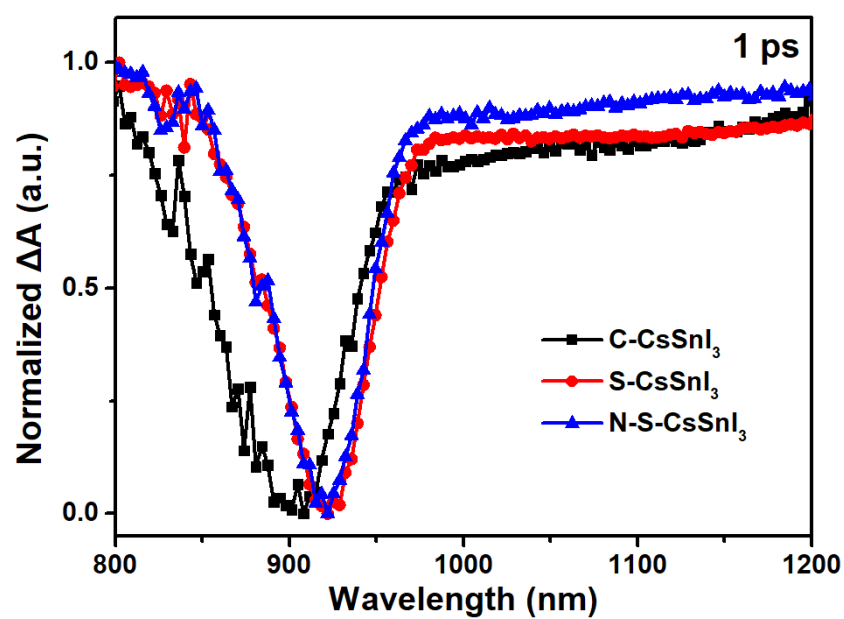
Supplementary Figure 30. TA spectra of CsSnI₃ films at different corresponding delay times (ps). C- (a), S- (b) and N-S-CsSnI₃ films (c).



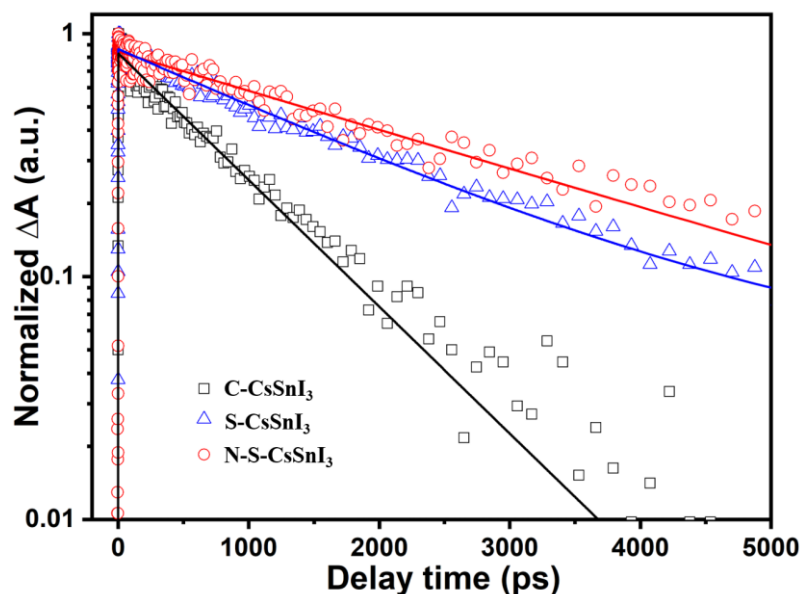
Supplementary Figure 31. (a) PB dynamics at 860 nm and 918 nm of C-CsSnI₃ films. (b) PB dynamics at 860 nm and 929 nm of S-CsSnI₃ films. (c) PB dynamics probed at 860 nm and 929 nm of N-S-CsSnI₃ films. The solid lines in all panels denote the fits.



Supplementary Figure 32. Normalized TA spectra of perovskite films prepared under different conditions at a corresponding delay time of 5 ps.



Supplementary Figure 33. Normalized TA spectra of CsSnI₃ films prepared under different conditions at a corresponding delay time of 1 ps.



Supplementary Figure 34. Kinetic traces of fs-TA spectra at probe wavelength of 918 nm for C-CsSnI₃ and 929 nm for S-CsSnI₃ and N-S-CsSnI₃ films. The solid lines denote the fits to a monoexponential decay function.

In the fs-TA spectra, following photoexcitation with 650 nm pump pulses at a fluence of 1.6 $\mu\text{J}/\text{cm}^2$, hot charge carriers are generated first and then rapidly relax to the band edge (Supplementary **Fig. 28-30**). The extracted hot charge carrier cooling times are 0.63 ± 0.04 ps for the C-, 0.62 ± 0.05 ps for S- and 0.62 ± 0.07 ps for N-S-CsSnI₃ films (Supplementary **Fig. 31**), respectively. The pseudocolor map of fs-TA spectra expressed as a function of both delay time and probe wavelength shows broadband photobleaching (PB) signals in the range from 800-1000 nm for C-CsSnI₃ films (Supplementary **Fig. 28**), while the N-S-CsSnI₃ films shows obvious narrowed PB signals and red-shifted band edge PB peaks (Supplementary **Fig. 29, 32, 33**), which agrees well with the absorption and PL spectra results. The band edge PB signals originates from the state-filling of the photogenerated carriers located near the band edge. The decay of the PB transients arises from electron-hole recombination as the band edge states becomes depopulated. The band edge PB decay kinetics can be well-fitted with a monoexponential decay function, and the extracted lifetime of N-S-CsSnI₃ films (2700 ± 100 ps) is much larger than that of the C- (830 ± 30 ps) and S-CsSnI₃ (1800 ± 100 ps) films (Supplementary **Fig. 34**), demonstrating that the charge carrier trapping from the band edge to the trap states is reduced with NPTU incorporation.

Notes for the DFT calculations: The density functional theory (DFT) computations were performed with the Vienna ab initio simulation package (VASP) ^[1-3] using the projector augmented-wave (PAW) method ^[4] with a plane wave cutoff ENCUT set to 500 eV. The recommended VASP PAW potentials for each element ^[5] were used for this study. We performed full structural relaxation with a convergence criterion of 10^{-8} eV for total energy in self-consistent field cycles and < 0.1 meV/Å for atomic forces. A k-point density of 0.12 Å^{-1} for structural relaxations and 0.10 Å^{-1} for accurate total energy calculations was used throughout via the KSPACING tag in VASP. The PBEsol ^[6] exchange-correlation functional was used for geometry optimization.

The rate of Auger recombination (R_{aug}) is defined using Fermi's golden rule as

$$R_{aug} = \frac{2\pi}{\hbar} \Sigma_{1234} |M_{1234}|^2 f_1 f_2 (1 - f_3)(1 - f_4) \delta(\epsilon_1 + \epsilon_2 - \epsilon_3 - \epsilon_4)$$

where $i = 1, 2, 3, 4$ represent the four single-particle states involved in the Auger processes, f_i are Fermi occupation factors, $i = [k, m]$ where k and m represent crystal momentum in reciprocal space and the band-index respectively and $M_{1234} = \langle \psi_1 \psi_2 | W | \psi_3 \psi_4 \rangle - \langle \psi_1 \psi_2 | W | \psi_4 \psi_3 \rangle$ is the antisymmetrized screened-Coulomb matrix element calculated using single-particle wavefunctions ψ_i .

We define the phase space volume for such processes as

$\Omega = \Sigma_{1234} f_1 f_2 (1 - f_3)(1 - f_4) \delta(\epsilon_1 + \epsilon_2 - \epsilon_3 - \epsilon_4)$ and utilize this quantity to perform a comparative study between compounds having similar electronic structures, as is the case in this work.

The calculation of available phase space volume for direct Auger recombination is carried out via dense sampling of the Brillouin zone using the HSE ^[7] functional with 50% exact Hartree-Fock

exchange. The amount of the exact-exchange has been chosen so the band-dispersions calculated via the HSE functional conform reasonably well with those calculated with the GW method^[8,9]. The delta function $\delta(\epsilon_1 + \epsilon_2 - \epsilon_3 - \epsilon_4)$ represents a product of two delta functions conserving energy and momentum respectively and has been implemented by approximating them as Gaussian functions with width, $\sigma = 0.20$ eV and $0.20 \text{ \AA}^{-1}$. For the calculation of Fermi occupation factors, the Fermi level is considered to be mid-gap, where the bandgap has been manually adjusted to represent experimental bandgaps of 1.3 eV for CsSnI₃ and 1.7 eV for CsPbI₃.

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- [3] G. Kresse et al. From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* **59**, 1758 (1999).
- [4] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* **50**, 17953 (1994).
- [5] Available PAW potentials, https://www.vasp.at/wiki/index.php/Available_PAW_potentials.
- [6] J. P. Perdew et al. Restoring the density-gradient expansion for exchange in solids and surfaces, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [7] Aliaksandr V. Krukau et al. Influence of the exchange screening parameter on the performance of screened hybrid functionals, *J. Chem. Phys.* **125** (22): 224106 (2006).
- [8] M. Shishkin et al. Implementation and performance of the frequency-dependent GW method within the PAW framework, *Phys. Rev. B* **74**, 035101(2006)
- [9] M. Shishkin et al. Self-consistent GW calculations for semiconductors and insulators, *Phys. Rev. B* **75**, 235102 (2007)

Notes for the carrier recombination dynamic simulations: We propose the following model (Eq. S1-S5) to describe the influence of the intrinsic p-doping characteristic and trap density on the charge carrier recombination dynamics of CsSnI₃ by simulating the evolution of free and trapped holes and electrons.

$$\frac{dn_e}{dt} = -k_{rad}n_en_h - k_{SRH}n_e(N_{te} - n_{te}) - k_{dt}n_en_{th} - k_{Au}(n_en_h^2 + n_hn_e^2) \quad (1)$$

$$\frac{dn_h}{dt} = -k_{rad}n_en_h - k_{SRH}n_h(N_{th} - n_{th}) - k_{dt}n_hn_{te} - k_{Au}(n_en_h^2 + n_hn_e^2) \quad (2)$$

$$\frac{dn_{te}}{dt} = k_{SRH}n_e(N_{te} - n_{te}) - k_{dt}n_hn_{te} \quad (3)$$

$$\frac{dn_{th}}{dt} = k_{SRH}n_h(N_{th} - n_{th}) - k_{dt}n_en_{th} \quad (4)$$

$$n_h = n_e + p_0 \quad (5)$$

In these equations, trap-mediated recombination channels with finite nature of trap numbers and carrier detrapping process are considered: n_e and n_h are the density of free electrons and holes, n_e included here is the initial value of " n_e " (equal to the excitation density), the initial condition on " n_h " should be the excitation density + doping; n_{te} and n_{th} are the density of trapped electrons and holes, N_{te} and N_{th} are the density of available electron and hole traps, p_0 is hole doping density; k_{rad} is the radiative recombination rate constant, k_{SRH} is the carrier trapping rate constant, k_{dt} is the detrapping rate constant of a trapped carrier with its free counterpart, k_{Au} is the Auger recombination rate constant. For the simulations, the parameters are $k_{Au}=10^{-28}$ cm⁶/s; $k_{rad}=10^{-9}$ cm³/s; $k_{SRH(e)}=10^{-10}$ cm³/s; $k_{SRH(h)}=10^{-9}$ cm³/s; $k_{dt(h)}=10^{-9}$ cm³/s; $k_{dt(e)}=10^{-12}$ cm³/s; $N_{te}=10^{15}$ cm⁻³; $k_{dt(e)}=10^{-12}$ cm³/s; the trap density changes from 10^{15} to 10^{18} cm⁻³, and the p-doping density changes from 10^{14} to 10^{20} cm⁻³. The time-dependent PL intensity can be described by equation S6. The carrier lifetime is extracted from the PL evolution with a delta function excitation and estimated as the time at which the PL intensity is decreased by a factor 1/e. The PLQY is the number of emitted photons normalized with respect to the excitation density as shown in equation S7.

$$n_{PL}(t) = k_{rad}n_e(t)n_h(t); n_{PL} = \int k_{rad}n_e(t)n_h(t)dt \quad (6)$$

$$PLQY = \frac{n_{PL}}{n} \quad (7)$$

Table 1. The fluorescence lifetimes of CsSnI₃ films prepared under different conditions.

Sample	A1(%)	t₁(ns)	A2(%)	t₂(ns)	T(ns)
C-CsSnI₃	3.2	1.4524	96.8	0.1298	0.49
S-CsSnI₃	100	1.3667	/	/	1.3667
N-S-CsSnI₃	100	2.2785	/	/	2.2785