Impact of photoluminescence reabsorption in metal-halide perovskite solar cells

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ABSTRACT: The precise quantification of the impact of photoluminescence reabsorption (PLr) in metal-halide perovskite solar cells (PSCs) has remained challenging. Here, the PLr effect is examined by combined time-resolved photoluminescence (TRPL) spectroscopy and time-resolved terahertz spectroscopy (TRTS) and a model is proposed which relates both the PLr and non-radiative recombination rate (k_{nr}) to the quasi-Fermi-level-splitting (QFLS). PLr is shown to be beneficial for the QFLS when k_{nr} is below a critical value of $\sim 7 \times 10^5 \text{ s}^{-1}$; at high k_{nr} PLr is detrimental to the QFLS. By incorporating PLr into a two-diode model that allows extraction of the effective k_{nr} , the series resistance (r_s), and the shunt resistance (r_{sh}) in PSCs, we find that

neglecting PLr overestimates the effective k_{nr} , while it does not affect the value of r_s and r_{sh} . Our findings provide insight into the impact of the PLr effect on metal-halide PSCs.

TOC GRAPHICS

Introduction

Photoluminescence reabsorption (PLr) describes the absorption of photons emitted by radiative carrier recombination in the photoactive layer itself.¹⁻⁵ Reabsorbed photons can be re-emitted successively; this process is also referred to as ‘photon recycling’. Different from photon management that increases the number of absorbed photons, for instance by surface texturing, index matching or by adding a back reflector, PLr is indirect and recursive and requires substantial overlap of the absorption and PL emission spectra (*i.e.* small Stokes shift).¹⁻³ Photoluminescence reabsorption has recently attracted significant attention to enhance the performance of perovskite solar cells (PSCs).¹⁻⁵ In PSCs it is facilitated by the perovskites’ small

Stokes shift, large absorption coefficient, small Urbach energy (typically <30 meV),⁶ and low defect densities, leading to predominantly radiative charge carrier recombination.⁷ It has been shown, that PLr prolongs the carrier lifetime and masks the intrinsic radiative recombination.⁴ Other works have shown that PLr is crucial to obtain high open-circuit voltages (V_{oc}).^{1,3} However, the quantification of PLr relies on numerical calculations, and its recursive behavior has remained elusive in PSCs.

Nonradiative recombination of charge carriers is another important process limiting the performance of PCSs. On the device level, high surface/interface recombination (SR) velocities are particularly detrimental to the V_{oc} , and they reduce the fill factor (FF) and the short-circuit current (J_{sc}). Although SR velocities in neat perovskite films are roughly 2-3 orders of magnitude lower compared to neat crystalline silicon (c-Si) and gallium arsenide (GaAs),^{9,10} surface passivation has proven to be critical in PSCs to achieve high power conversion efficiency (PCE).¹¹⁻¹⁹ Whereas the amount of SR and its impact on V_{oc} can experimentally be controlled very well, the quantification of the effective non-radiative recombination rate (k_{nr}) is still challenging, mainly hampered by the PLr effect. Therefore, a strategy to quantify PLr is of utmost importance.

In this work, we propose an approximate analytical solution of PLr based on one dimensional photon diffusion theory, enabling us to quantify the contribution of PLr to the total charge-carrier recombination; in other words, we reveal its impact on the carrier evolution after pulsed photoexcitation, and the carrier density buildup under continuous illumination. We examine the classic $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MA) and the state-of-the-art triple-cation mixed $\text{FA}_{0.81}\text{MA}_{0.14}\text{Cs}_{0.05}\text{PbI}_{2.55}\text{Br}_{0.45}$ (FAMACs) in thin films by both photoluminescence (PL) spectroscopy and time-resolved terahertz spectroscopy (TRTS). We then propose a model to relate PLr and nonradiative recombination to the quasi-Fermi-level-splitting (QFLS), which sets the

ceiling of the V_{oc} ,²⁰ and we extract the effective k_{nr} in non-passivated FAMAC PSCs and interface-passivated PSCs, which have demonstrated better reproducibility of device performances with improved phase stability.^{21, 22} Finally, we reveal that PLr is detrimental to the QFLS at high k_{nr} , but beneficial to QFLS, when k_{nr} is smaller than a ‘critical’ value of $\sim 7 \times 10^5 \text{ s}^{-1}$. By fitting the devices’ J - V curves,²³ we find that neglecting PLr overestimates the effective k_{nr} , but it hardly affects the series resistance (r_s) and shunt resistance (r_{sh}). Moreover, r_s decreases and r_{sh} increases with passivation, indicating the interface contact properties are improved and interface current leakage is suppressed by passivation. Our findings demonstrate the importance to consider the PLr effect in metal-halide PCSs.

Results

Dimensionless solution of the PLr ratio

A strategy to determine the maximum available V_{oc} of a PSC is to quantify the perovskite film’s PL quantum efficiency (PLQE, η_{ext}),²⁴ where η_{ext} is defined as the ratio of photons emitted over photons absorbed by the photoactive layer. Although the emitted photons do not contribute to V_{oc} , η_{ext} acts as an indicator of the radiative recombination efficiency that depends on the density of photo-excited carriers, as described by quasi-Fermi-level-splitting (QFLS) and the charge carrier’s temperature.²⁵ In the idealized open circuit case, the intimate relation between V_{oc} and η_{ext} is represented by $qV_{oc} = \mu_{rad} + k_B T \ln(\eta_{ext})$,²⁴ where μ_{rad} is the QFLS at the radiative limit (*i.e.* only radiative recombination occurs), k_B is the Boltzmann constant, and T is the temperature. Besides determining PLQE experimentally,²⁶ η_{ext} can be extracted from the internal PLQE (η_{int}), when all radiative and non-radiative recombination constants are known^{2,3}. However, recursive photon absorption and emission add complexity to the problem. Generally, η_{ext} and η_{int}

obey a non-linear relation when PLr is present.² Here, we employ the photon diffusion theory to establish such a relation.

Room-temperature absorption and steady-state PL spectra of the two perovskite thin film samples (MA: $d \sim 300$ nm and FAMACs: $d \sim 600$ nm) are shown in Fig. 1a. The large overlap between the absorption and the PL spectra (*i.e.* small Stokes shift) facilitates efficient PLr in both samples, especially when photons are emitted in the bulk and travel across longer distances in the photoactive layer. In the presence of PLr, each PL photon has a certain probability to be re-absorbed and re-emitted. In the simplest case that the photon current is restricted in one dimension along the sample thickness, the PL photon density (γ) can be described by the photon diffusion equation:^{1,27}

$$\frac{\partial \gamma(x, t, \lambda)}{\partial t} = D_\lambda \frac{\partial^2 \gamma}{\partial x^2} + k_2 n(x, t)^2 g_\lambda - \frac{c}{n_s} \alpha_\lambda \gamma \quad (1)$$

where c , n_s , α_λ are the speed of light, perovskite's refractive index and absorption coefficient, respectively. Further, D_λ is the photon diffusion/propagation coefficient that results from photon scattering/transport,²⁷ k_2 and n represent the bimolecular recombination rate and the density of excited free carriers, respectively. Since the radiative recombination is dominated by $k_2 n^2$ in perovskites,²⁸ the intrinsic PL emission rate (R_{PL}) is set to $k_2 n^2 g_\lambda$ with g_λ being the spectral distribution of intrinsic emission. The last term represents the photon depletion rate through PLr (or carrier generation rate due to PLr, that is, the PLr rate). Although Eqn. 1 is coupled to the carrier density (n), we can solve it separately under the condition that photon diffusion is much faster than carrier diffusion, which is a valid approximation in metal-halide perovskites. Hence, the general solution of the PLr rate for one PLr cycle is (see Eqn. S7 in SI):

$$G_{PLr0}(x, t, \lambda) = \alpha_\lambda \int_0^d \frac{R_{PL}(y, t, \lambda)}{2} e^{-\alpha_\lambda |x-y|} dy \quad (2)$$

where d is the thickness of the perovskite film. The denominator 2 accounts for the two propagation directions of the photons in one dimension. The exponential decay indicates PLr is governed by Lambert-Beer's absorption law, due to the small scattering coefficient.⁴

Figure 1. Photoluminescence reabsorption and photoluminescence measurements. (a) The large overlap between the absorption spectra (left axis) and the steady-state photoluminescence (PL) spectra (right axis) indicates strong photoluminescence reabsorption (PLr). (b) A schematic of escape cones and different photon modes. Photons in the escape mode leave the film directly; photons in leaky modes leave the film after one internal reflection; photons in guided modes are trapped by total internal reflection. (c) The distribution of PLr-induced carrier generation rate is nearly uniform (dashed lines), if the carrier distribution is constant. However, for an exponential distribution $n_{exp}(x)$, the PLr-induced carriers are distributed exponentially, but deeper (solid lines) into the perovskite film, indicating carrier redistribution. (d) The PLr efficiency (η_{PLr}) integrated

from (c) over x has a weak dependence on film thickness and carrier distribution, but its components depend on film thickness and carrier distribution. (e) Top panel: measured PL spectra upon bulk excitation (PL_{ext}) and the modeled intrinsic PL spectra (PL_{ext0}). Middle panel: excitonic resonance energy gap (E_g) extracted from the absorption spectra using the Elliott model including continuum absorption α_{con} and excitonic absorption α_{exc} . Bottom panel: the same steady-state PL spectra as in (a). The modeled PL_{ext0} peaks close to E_g as expected.

However, the aforementioned solution is incomplete, because internal reflections are neglected. For photons in a planar perovskite film, the perovskite's large refractive index ($n_s \sim 2.6$) leads to two escape cones (Fig. 1b). Photons with directions beyond the escape cones undergo internal reflection and contribute to both the leaky modes and guided modes, depending on the critical angle (θ_c) of total internal reflection at the front surface (θ_{c1}) and back surface (θ_{c2}). The probability that PL photons enter the escape cones can be described by $(1 - \cos\theta_c)/2$, which is the ratio of the escape cone over the solid angle of the sphere. The estimated escape probability is $\sim 4\%$ for the perovskite/air interface ($\theta_{c1} \sim 23^\circ$) and $\sim 7\%$ for the perovskite/quartz interface ($\theta_{c2} \sim 30^\circ$), leading to very efficient internal reflections. In the strong reflection regime, the solution of Eqn. 1 can be approximated by adding image sources as boundary conditions.²⁹ With this, and by integrating over the solid angle, the PLr rate through leaky and guided modes, respectively, are given by (see Eqn. S9-S10 in SI):

$$G_{lek}(x, t, \lambda) = \alpha_\lambda \int_0^d \int_{\theta_{c1}}^{\theta_{c2}} \frac{R_{PL}(y, t, \lambda) \sin \theta}{2} e^{-a_\lambda l} d\theta dy \quad (3a)$$

$$G_{gd}(x, t, \lambda) = f_{mc} \alpha_\lambda \int_0^d \int_{\theta_{c2}}^{\pi/2} \frac{R_{PL}(y, t, \lambda) \sin \theta}{2} e^{-a_\lambda l} d\theta dy \quad (3b)$$

where l is the distance between x and the image sources, f_{mc} is a coefficient that accounts for the microcavity effect in thin films.³⁰ When neglecting the internal reflection in the escape cones, the total PLr rate becomes:

$$G_{PLr}(x, t, \lambda) = G_{PLr0}(x, t, \lambda) + G_{lek}(x, t, \lambda) + G_{gd}(x, t, \lambda) \quad (4)$$

The fraction of G_{PLr} among all the intrinsic R_{PL} is shown in Fig. 1c, classified by the cases of constant distribution (n_{con}) and exponential distribution (n_{exp}). In the n_{con} case, G_{PLr} is nearly constant everywhere; in contrast, in the case of n_{exp} , G_{PLr} has a positive correlation to the carrier density, that is, the area with higher carrier density reabsorbs more photons. We find G_{PLr} extends much deeper into the film than n_{exp} , indicating PLr introduces carrier redistribution (Fig. 1c). However, this redistribution is negligible when compared to the redistribution by carrier diffusion (See Sec.2 in SI). The overall PLr efficiency (η_{PLr}) can be obtained by integrating G_{PLr} over x , yielding $\sim 87.4\%$ and $\sim 90.7\%$ for MA and FAMACs, respectively (Fig. 1d). Interestingly, MA has a comparable η_{PLr} with FAMACs, whereas its thickness is only half. By disentangling the PLr efficiency contribution by G_{PLr0} (η_{PLr0} , contributions without internal reflections), leaky modes (η_{lek}) and guided modes (η_{gd}), we find η_{PLr0} expectantly, increases with thickness. However, as η_{gd} depends on the photon density in the guided modes that is attenuated by G_{PLr0} , its relation is opposite. Besides the weak thickness-dependence of η_{PLr} , we find η_{PLr} is independent of carrier diffusion, if the distribution is exponential (Fig. 1d). Therefore, η_{PLr} can be further simplified, if the absorption spectrum changes linearly with wavelength in the PL region (see Sec. 4 in SI), which is the case in metal-halide perovskite films (Fig. 1a):

$$\eta_{PLr} \cong 1 - [1 - |f_1 - f_2|(1 - e^{-\alpha_{PL}d})/2 - \min(f_1, f_2)f_{mc}] \frac{1 - e^{-\alpha_{PL}d}}{\alpha_{PL}d} \quad (5)$$

where $f_1 = 1 - \cos \theta_{c1}$ and $f_2 = 1 - \cos \theta_{c2}$. α_{PL} is the absorption coefficient at the PL peak.

Since photons at wavelengths corresponding to higher absorption coefficients are readily reabsorbed, the external PL spectrum should exhibit a red shift when compared with the intrinsic PL spectrum,^{4,31} which can be estimated from the exponential reabsorption behavior revealed by Eqn. 2. For low fluence bulk-excited PL, the external PL flux without the PLr effect (PL_{ext0}) at the front interface ($x=0$) is related to the measured external PL flux (PL_{ext}) by (see Sec. 4 in SI):

$$\frac{PL_{ext}(\lambda)}{PL_{ext0}(\lambda)} \cong \frac{1 - e^{-\alpha_\lambda d}}{\alpha_\lambda d} \quad (6)$$

This relation enables us to reveal the intrinsic PL emission based on time-resolved PL spectroscopy (TR-PL) and steady-state PL spectroscopy. The top panel of Fig. 1e shows the normalized TR-PL spectra obtained at 5 ns and 20 ns after photoexcitation. At these two time points, excited carriers exhibit a quasi-uniform distribution along the film thickness due to their high mobilities.^{9,32} The normalized spectra at two time points are almost identical in MA, but a small redshift exists in FAMACs, which could be induced by relaxation and band-filling.³³ As the PL intensity can be scaled to the external PL flux assuming Lambert's cosine behavior,²⁶ we can directly use the normalized values of the TR-PL spectra as experimental PL_{ext} to calculate PL_{ext0} . By comparing to the Elliott analysis of the absorption spectra^{28,34} (see Sec. 3 in SI), we find PL_{ext0} peaks in between the exciton resonance and the band-to-band transition (middle panel in Fig. 1e), indicating that ionized electron-hole plasma dominates the photo-excited species, consistent with earlier reports.²⁸ In the steady-state PL obtained by 532 nm excitation (bottom panel in Fig. 1e), the redshift of the spectrum due to PLr is not expected, because carriers are excited near the surface. However, the spectra of both samples are red-shifted when compared to PL_{ext0} determined by TR-PL. This is mainly because carrier diffusion can cause a significant redistribution in thin films. Other mechanisms could also contribute to the observed redshift, for instance light soaking.³⁵ However, this effect is ruled out based on the time-dependent PL experiments (see Sec. 2 in SI).

Our calculation confirms that the redistributed carrier density is nearly constant in the samples (see Sec. 2 in SI), consequently Eqn. 6 is applicable to the steady-state PL. Again, PL_{ext0} calculated from steady-state PL peaks in between the exciton resonance and the band-to-band transition.

Contradictory reports exist on the impact of PLr on PLQE: it has been shown that the apparent radiative recombination is suppressed by PLr,⁴ implying a decrease of the external PLQE (η_{ext}), while, PLr-enhanced η_{ext} has been demonstrated as well.² Indeed, PLr is typically considered a loss mechanism, because the reabsorption attenuates the PL emission. However, a fraction of the reabsorbed photons can be re-emitted into the escape cones in the next PLr cycle,³ and thus the fraction increases with the internal PLQE (η_{int}). On the other hand, PLr acts as an extra excitation source that increases the carrier density (Δn), thus suppression of non-radiative losses is expected, especially in the case of efficient photon recycling.¹⁻³ Therefore, η_{ext} is determined by the tradeoff between PLr attenuation and PLr-induced carrier buildup. Since photons either escape or are reabsorbed, η_{ext} can be represented by (see SFig. 7 in SI):

$$\eta_{ext}^{NoPLr} = \eta_{oc}\eta_{int0}, \quad \eta_{int0} = \frac{k_2 n_0^2}{k_2 n_0^2 + R_{nr}(n_0)} \quad (7a)$$

$$\eta_{ext}^{PLr} = \frac{(1 - \eta_{PLr})\eta_{int}}{1 - \eta_{PLr}\eta_{int}}, \quad \eta_{int} = \frac{k_2 n_{eq}^2}{k_2 n_{eq}^2 + R_{nr}(n_{eq})} \quad (7b)$$

where η_{oc} is the outcoupling limit determined by the escape cones (see Eqn. S13 in SI); n_0 is the initial carrier density without PLr; R_{nr} describes the non-radiative recombination caused by trap-assisted recombination or/and Auger recombination; $n_{eq}=n_0+\Delta n$ is the PLr-induced quasi-equilibrium carrier density. Here η_{ext} is defined as the fraction of external photons among the absorbed photons. In real devices, η_{ext} is also reduced by energy loss due to surface reflection and parasitic absorption. According to the numerator in Eqn. 7b, the presence of η_{PLr} reduces η_{ext} , which implies that materials with weaker PLr could be suitable for both light-emitting-diodes

(LEDs) and solar cells. However, Δn obtained from the photon recycling can increase η_{int} . Therefore, PLr can assist η_{ext} to exceed the outcoupling limit, and even $\eta_{ext}=100\%$ can be expected (when $\eta_{int}\rightarrow 1$). In general, PLr is detrimental for η_{ext} at low η_{int} , but this negative impact gradually ceases when η_{int} increases.⁵

Determination of intrinsic radiative recombination rate

To extract η_{ext} by the method mentioned above, it is critical to get the intrinsic value of the radiative recombination rate k_2 . Our approach here is to determine it by fitting fluence-dependent TRTS dynamics.³⁶⁻³⁹ A schematic of our TRTS experiment is shown in Fig. 2a. Further details are presented in the SI. TRTS measures the time evolution of a terahertz electrical field after photoexcitation with sub-picosecond time resolution. The signal amplitude is a direct measure of the electron mobility (μ_n), hole mobility (μ_p), and photo-generated carrier density (n) according to:

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$$\frac{\Delta E(t)}{E_0} = -\frac{1}{\epsilon_0 c (n_A + n_B)} \int_0^d \Delta \sigma(x, t) dx, \quad \Delta \sigma = (\mu_n + \mu_p) q \varphi n \quad (8)$$

where d is the sample thickness, $\Delta \sigma$ the photo-induced change of photoconductivity, ϵ_0 the dielectric constant of vacuum, c the speed of light, and n_A and n_B the refractive indexes of the surrounding materials, q the unit charge, and φ the quantum yield of free carriers. The quantum yield φ is used as a coefficient ($0 \leq \varphi \leq 1$), since our TRTS is not sensitive to excitons with a binding energy larger than the terahertz photon energy (the upper limit of our setup is 3 THz $\sim$ 12.3 meV). Here we assume $\varphi \sim 1$, implying that free carriers are the dominant species generated by photoexcitation in the range of carrier densities we are interested in, supported by the quadratic density dependence of the spontaneous photon emission.²⁶ Fluence-dependent TRTS

measurements were performed to study the carrier dynamics of MA films ($d \sim 300$ nm) and FAMACs films ($d \sim 600$ nm) (Fig. 2b). Samples were photo-excited at 550 nm (pulse width ~ 120 fs) at room temperature, and all experiments were performed under nitrogen atmosphere to avoid degradation. The summation of $\mu_n + \mu_p$ extracted from the peak value of TRTS kinetics is shown in Fig. 2c. The measurements on both samples show that the carrier mobility has no obvious excitation fluence dependence, indicating that, when the TRTS signal reaches its maximum amplitude,³⁸ the THz photoconductivity can be considered as only affected by the recombination of free carriers (Eqn. 8).

Figure 2. Time-resolved terahertz spectroscopy (TRTS) measurements. (a) Schematic of optical pulses incident on the perovskite sample. The pump laser pulse is incident to the sample's top surface, while the terahertz probe pulse is incident to the backside. (b) Sum of electron and hole mobilities in MA and FAMACs thin films after photoexcitation with different pump fluence. The dashed line is the average mobility in the regime where TRTS exhibits a linear response to

the pump fluence ($<30 \mu\text{J}/\text{cm}^2$). **(c)** Fluence-dependent TRTS kinetics and global fits using the rate equation described in the main text. The fitting parameters are shown in Tab. 1. **(d)** TR-PL kinetics of both perovskite samples. Both decays can be fitted by two-exponential fits. The slower decay component τ_2 is indicated by the dashed line. **(e)** The internal PLQE and external PLQE plotted against carrier density, based on the recombination constants obtained from the TRTS fits. PLr improves η_{ext} when $\eta_{int}>50\%$. It assists η_{ext} to overcome the outcoupling limit (OC limit) when $\eta_{int}>70\%$.

Next, we investigate the carrier dynamics. As the diameter of the terahertz beam (here: 1.6 mm) is significantly larger than the perovskite layer thickness, the problem is limited to one-dimensional diffusion of carriers across the layer. Hence, the general rate equation including free-carrier diffusion accounting for SR and PLr becomes: ^{1,25}

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - k_1 n - k_2 n^2 - k_3 n^3 + G_0 + G_{PLr} \quad (9)$$

where $n(x, t)$ is the carrier density at point x along the perovskite film thickness, D is the ambipolar diffusion coefficient related to the ambipolar mobility μ_a via the Einstein relation, $D = \mu_a k_B T / q$, where μ_a can be assessed from the measured $\mu_n + \mu_p$ by $2/\mu_a = 1/\mu_n + 1/\mu_p$ with a known μ_p/μ_n (or μ_n/μ_p), which was reported to be 1~11.3 for MA and 1~26 for FAMACs perovskite films. ^{32,40} Further, k_1 is the recombination rate assigned to trap states, defects, or impurities in the bulk, k_2 is the radiative recombination rate, k_3 is the Auger recombination rate, $G_0(x) = n_0 e^{-a_p x}$ is the initial carrier density generated by pulsed excitation (see Sec. 6 in SI), and G_{PLr} is the carrier generation rate due to PLr represented by Eqn. 2-4. To account for SR, we use the following boundary conditions: ^{9,10}

$$D \frac{\partial n}{\partial x} \Big|_{x=0} = S_0 n, \quad D \frac{\partial n}{\partial x} \Big|_{x=d} = -S_d n, \quad (10)$$

where S_0 and S_d are the SR velocities at the front ($x = 0$) and back ($x = d$) sides of the perovskite layer, respectively, for simplicity we set $S_0=S_d=S$ as also suggested by others.^{9,10} Here the boundary conditions only account for the surface of the film. Since the average grain size in both samples is ~ 300 nm (see Sec. 1 in SI), grain-boundary recombination in FAMACs can contribute to k_1 . We show that it is possible to find the upper limit of S from the TR-PL kinetics. By parametrizing the TR-PL kinetics with two-exponential fits (Fig. 2d), we obtained the longer decay component τ_2 , which has previously been assigned to mono-molecular recombination,³⁶ leading to an effective $k_{1eff}=1/(2\tau_2)$. k_{1eff} is related to the intrinsic k_1 and SR rate (k_s) by $k_{1eff}=k_1+k_s$, that is, $k_s \leq k_{1eff}$. The upper limit of S was estimated from k_{1s} by:⁴¹

$$\frac{1}{k_s} = \frac{d}{2S} + \frac{1}{D} \left(\frac{d}{\pi} \right)^2 \quad (11)$$

It is noteworthy that Eqn. 10 only holds for low level injection where mono-molecular recombination dominates, which is the case in our TR-PL measurements (Fig. 2d). Using $D \sim 0.5(\mu_n + \mu_p)k_B T/q$, the upper limit of S is ~ 73.3 cm/s and 149.3 cm/s for MA film and FAMACs film, respectively.

Since the change in the photoconductivity is mainly induced by changes of the carrier density (see Eqn. 8), the fluence-dependent TRTS kinetics can be fitted globally using Eqn. 9. The experimental data was described well when setting μ_p/μ_n , k_2 and k_3 as free parameters, while fixing S to different values. Here k_1 was obtained from k_{1eff} using $k_{1eff}=k_1+k_s$ and Eqn. 11. The best fits are shown in Fig. 2c. Because k_1 and S contribute on a larger time scale (~ 100 ns) beyond our TRTS window (~ 3.5 ns), we could not discern the value of S . However, we consider the fitted k_2 reliable, because its dependence on S is small (Tab. 1). The fitted k_2 is the intrinsic value, since the

PLr-generated carriers are taken into account. For further analysis of the fitted k_2 , we present the onset density of the power dependence of the TRTS (n_{pd}) in Table 1 together with the ratio of PLr-induced carrier diffusion and intrinsic carrier diffusion (D_{PLr}/D). The values are consistent with experimental observations (see Sec.6 in SI), indicating that $k_2 \sim 2 \times 10^{-10}$ and $\mu_p/\mu_n \sim 1.05$ in both MA and FAMACs films.

Table 1: Results of fits to the experimental TR-PL and TRTS kinetics. Numbers in bold are the main outputs.

Input	S (cm/s)	MA			FAMACs		
		0	25	50	0	60	120
TR-PL	$1/k_{1eff}$ (ns)	260.74 $\pm$ 12.10	260.74 $\pm$ 12.10	260.74 $\pm$ 12.10	205.46 $\pm$ 2.18	205.46 $\pm$ 2.18	205.46 $\pm$ 2.18
TRTS	$\mu_n + \mu_p$ (cm ² /V/s)	17.77 $\pm$ 0.31	17.77 $\pm$ 0.31	17.77 $\pm$ 0.31	13.18 $\pm$ 0.09	13.18 $\pm$ 0.09	13.18 $\pm$ 0.09
	k_2 (cm ³ /s)	(3.19 $\pm$ 0.11) $\times 10^{-10}$	(2.65 $\pm$ 0.09) $\times 10^{-10}$	(2.25$\pm$0.10)$\times 10^{-10}$	(6.51 $\pm$ 0.17) $\times 10^{-10}$	(4.45 $\pm$ 0.22) $\times 10^{-10}$	(1.51$\pm$0.28)$\times 10^{-10}$
	k_3 (cm ⁶ /s)	(6.65 $\pm$ 0.13) $\times 10^{-29}$	(6.83 $\pm$ 0.11) $\times 10^{-29}$	(6.89 $\pm$ 0.10) $\times 10^{-29}$	(8.45 $\pm$ 0.18) $\times 10^{-29}$	(8.24 $\pm$ 0.16) $\times 10^{-29}$	(7.79 $\pm$ 0.21) $\times 10^{-29}$
	μ_p/μ_n	1.09 $\pm$ 0.09	1.07 $\pm$ 0.07	1.06$\pm$0.06	1.12 $\pm$ 0.12	1.07 $\pm$ 0.07	1.05$\pm$0.05
Output	k_s (s ⁻¹)	0	1.67 $\times 10^6$	3.34 $\times 10^6$	0	2.01 $\times 10^6$	4.04 $\times 10^6$
	k_1 (s ⁻¹)	3.84 $\times 10^6$	2.17 $\times 10^6$	0.50 $\times 10^6$	4.85 $\times 10^6$	2.84 $\times 10^6$	0.81 $\times 10^6$
	D (cm ² /s)	0.212 $\pm$ 0.010	0.215 $\pm$ 0.007	0.216 $\pm$ 0.006	0.156 $\pm$ 0.009	0.159 $\pm$ 0.006	0.160 $\pm$ 0.004
	$L = \sqrt{D/k_1}$ (nm)	2352.0 $\pm$ 55.7	3149.7 $\pm$ 53.1	6583.2 $\pm$ 105.2	1789.1 $\pm$ 54.6	2370.3 $\pm$ 38.7	4451.0 $\pm$ 51.1
	n_{pd} (cm ⁻³)	0.95 $\times 10^{17}$	1.15 $\times 10^{17}$	1.35 $\times 10^{17}$	0.80 $\times 10^{17}$	1.17 $\times 10^{17}$	3.46 $\times 10^{17}$
	D_{PLr}/D	25.00%	20.48%	17.35%	67.51%	44.83%	15.05%

Since it is difficult to differentiate between the hole and electron mobility, the ratio of μ_p/μ_n can also be μ_n/μ_p . However, we consider electrons to be the slower carriers, as also suggested earlier by others.⁴⁰ By using the average rate constants of two samples, that is, $\mu_p/\mu_n \sim 1.06$, $\mu_p + \mu_n \sim 15$ cm²/V/s, $k_{1eff} \sim 8 \times 10^6$ s⁻¹, $k_2 \sim 2 \times 10^{-10}$ cm³/s, and $k_3 \sim 7.5 \times 10^{-29}$ cm⁶/s, we plot η_{int} and η_{ext} including and excluding PLr in Fig. 2e. Here, the effect of PLr is observed very clearly. When η_{int} is lower

than ~50%, PLr reduces η_{ext} ; when η_{int} is higher than ~70%, PLr assists η_{ext} to overcome the OC limit. We find the carrier density for η_{int} ~50% to be $\sim 4 \times 10^{16} \text{ cm}^{-3}$, which exceeds the carrier density in PSCs under 1-Sun illumination ($\sim 10^{13}$ - 10^{16} cm^{-3}). However, the perovskite samples used here are without passivation. In fact, after careful surface and/or bulk passivation, η_{int} >90% and η_{ext} ~43% has been obtained experimentally in perovskite films under 1-sun illumination,^{11,24} providing the possibility to use PLr to improve η_{ext} and further increase V_{oc} .

Quantification of the PLr effect on QFLS

Based on the PLr solution and the intrinsic value of k_2 discussed above, we are able to quantify the PLr effect on the perovskite's QFLS (μ_{PVK}) in PSCs, which sets the ceiling for the V_{oc} .²⁰ Our approach leading to the determination of μ_{PVK} is to estimate the equilibrium carrier density (n_{eq}) and η_{ext} under 1-sun illumination. A scheme of a typical *n-i-p* PSC is shown in Fig. 3a. The work-function difference between the electrodes results in a built-in electrical field (E) across the perovskite film, spatially separating the photo-generated carriers, driving them to the respective charge-selective interfaces. However, the electron-transport layer (ETL) and hole-transport layer (HTL) are not perfect, carrier recombination occurs at the respective interfaces⁴² (Fig. 3a). Furthermore, ions can accumulate at the interface, which reduces E and introduces recombination centers.⁴³⁻⁴⁵ For simplicity, we use k_{nr} to account for the effective non-radiative recombination rate that originates from the perovskite bulk and the interfaces. The purpose of interface passivation is to reduce k_{nr} either by adding interlayers or through interface engineering.¹⁸

Starting from a sample stack as shown in Fig. 3a, we define $f_1=1-\cos 30^\circ \sim 86\%$ to account for the escape cone at the perovskite/ETL/ITO side, and $f_2=96\%$ to account for back reflection from the

Au layer (reflectivity of Au is ~96%). Hence, η_{PLr} can be determined by Eqn. 5. Under V_{oc} conditions, the carrier generation and recombination are balanced according to:

$$G_{PLr} + G_0 = k_{nr}n_{eq} + k_2n_{eq}^2 \quad (12)$$

where $G_{PLr} \sim \eta_{PLr}k_2n_{eq}^2$ is the carrier generation due to PLr, and G_0 is the carrier generation rate due to photoexcitation. Under 1-sun illumination, we consider non-radiative recombination as a first order recombination process, since Auger recombination is negligible under these conditions.

G_0 can be obtained by summation over the AM1.5G photon fluence spectrum, $G_0^{1sun} = \sum_{\lambda} AM1.5G \cdot (1 - O_{\lambda})(1 - e^{-2\alpha_{\lambda}d})/d$, where O_{λ} is the optical loss accounting for the front reflection and the parasitic absorption; $2\alpha_{\lambda}d$ accounts for the of Au back mirror. We note that here the generation profile is not considered, because neither QFLS nor V_{oc} depend significantly on the generation profile due to the carriers' rapid diffusion.⁴⁶ With the assumption of unity internal quantum efficiency (IQE=1), we can estimate O_{λ} by $(1 - O_{\lambda})(1 - e^{-2\alpha_{\lambda}d}) = EQE_{\lambda}$, where EQE is the external quantum efficiency of the PSC device (see Fig. S2 in SI). Therefore, alternative expressions of η_{ext} can be obtained:

$$\eta_{ext}^{NoPLr} = \frac{\eta_{oc}k_2n_{eq}^2}{G_0}, \quad \eta_{ext}^{PLr} = \frac{(1 - \eta_{PLr})k_2n_{eq}^2}{G_0} \quad (13)$$

These equations are equivalent to Eqn. 7 when replacing G_0 with $k_{nr}n_{eq} + k_2n_{eq}^2 - G_{PLr}$. Since the energy of PL photons is much greater than $k_B T$, μ_{rad} and QFLS can be approximated as²⁶:

$$G_0^{1Sun}d \cong \int Y(\lambda, d) e^{-\frac{hc/\lambda - \mu_{rad}}{k_B T}} d\lambda \quad (14a)$$

$$(1 - \eta_{PLr})k_2n_{eq}^2d \cong \int Y(\lambda, d) e^{-\frac{hc/\lambda - \mu_{PVK}}{k_B T}} d\lambda \quad (14b)$$

$$(1 - \eta_{PLr})k_2n_i^2d \cong \int Y(\lambda, d) e^{-\frac{hc/\lambda}{k_B T}} d\lambda \quad (14c)$$

$$Y(\lambda, d) = \frac{2\pi hc^2}{\lambda^5} (1 - O_{\lambda})(1 - e^{-2\alpha_{\lambda}d}) = \frac{2\pi hc^2}{\lambda^5} EQE_{\lambda} \quad (14d)$$

$\mu_{PVK} = \mu_{rad} + k_B T \ln(\eta_{ext})$ can be directly derived from Eqn. 14a and Eqn. 14b by using Eqn. 13. In

the case of $\mu_{PVK}=0$, an intrinsic carrier density $n_i \sim 1 \times 10^5 \text{ cm}^{-3}$ is determined by Eqn. 14c.

Figure 3. Impact of PLr and interface recombination on V_{oc} and fit to the experimental J - V characteristics. (a) In a typical n - i - p type PSC, the interface recombination is the main nonradiative recombination pathway. (b) Simulated equilibrium carrier density (n_{eq}) under 1-sun illumination for different perovskite thicknesses and non-radiative recombination rates. Dashed lines correspond to the absence of PLr. (c) Corresponding simulated internal PLQE (η_{int}) and external PLQE (η_{ext}). PLr can aid η_{ext} in overcoming the outcoupling limit (OC limit) at $k_{nr}=10^5 \text{ s}^{-1}$. (d) Corresponding simulated QFLS and the maximum QFLS below the radiative limit. Filled triangle (passivation-2), circle (passivation-1), and square (control), respectively, represent V_{oc} of the three types of PSCs, indicating k_{nr} obtains values in between 10^6 s^{-1} and 10^7 s^{-1} in our PSCs. (e) Simulated QFLS for PSCs with perovskite thickness of 600 nm under 1-sun illumination. (f)

Fits to the J - V curve of passivation-2 PSCs. Dashed lines are J - V curve predictions, assuming zero series resistance ($r_s=0$) and infinite shunt resistance ($r_{sh}=\infty$) in $\text{Ohm}\cdot\text{cm}^2$, respectively.

The thickness-dependent n_{eq} and the corresponding η_{int} and η_{ext} under 1-sun illumination for a series of k_{nr} are shown in Fig. 3b and 3c. For all investigated thicknesses, n_{eq} increases as k_{nr} decreases as expected. Because $G_{PLr} \sim \eta_{PLr} k_2 n_{eq}^2$ is proportional to n_{eq}^2 , the PLr-induced carrier buildup is observed only at low k_{nr} (Fig. 3b), providing higher η_{int} than in the case of no PLr (left panel in Fig. 3c). With the assistance of PLr, η_{ext} exceeds η_{oc} and even $\eta_{ext} \rightarrow 100\%$ can be achieved under 1-sun condition (right panel in Fig. 3c). We note that for simplicity, η_{ext} is defined as the fraction of the number of incident photons divided by the number of absorbed photons. Thus, for the experimentally-determined external PLQE across the entire 1-sun spectrum, η_{ext} should be scaled by $G_0^{1sun} d / \sum_{\lambda} \text{AM1.5G}$ to account for the optical loss due to surface reflections, parasitic absorption, and transmission.

The calculated μ_{rad} (radiative limit) and μ_{PVK} are plotted in Fig. 3d. Clearly, passivation of non-radiative recombination centers is essential to achieve high μ_{PVK} in PSCs. We find μ_{PVK} is optimal for thicknesses of ~ 300 nm, ~ 600 nm, and ~ 900 nm. This is a consequence of the thickness-dependent microcavity effect, which enhances η_{ext} at λ/n_s , $2\lambda/n_s$, and $3\lambda/n_s$ ²⁸. The same effect is essential for perovskite LEDs,² its importance for PSCs has not been confirmed yet. PLr is detrimental to μ_{PVK} at high k_{nr} , while beneficial to μ_{PVK} , when k_{nr} is smaller than a critical value of $\sim 7 \times 10^5 \text{ s}^{-1}$ (Fig. 3e). This value becomes larger, when we use larger $\eta_{PLr} k_2$ in the simulation. The impact of PLr on μ_{PVK} is seen in Fig. 3e, where the k_{nr} -dependent μ_{PVK} for PSCs with $d=600$ nm is shown. Ideally, PLr can lead to an increase in μ_{PVK} of ~ 40 meV, when $k_{nr}=10^4 \text{ s}^{-1}$. When k_{nr} exceeds $\sim 10^6 \text{ s}^{-1}$, μ_{PVK} becomes proportional to the logarithm of k_{nr} regardless of the PLr effect

(Fig. 3e). From Eqn. 12, 14b and Eqn. 14c, we can estimate the μ_{PVK} increase caused by passivation:

$$\Delta\mu_{PVK} \cong 4.6V_T \log_{10} \frac{k_{nr}}{k'_{nr}} \quad (15)$$

where $V_T = k_B T / q$ and k'_{nr} are the thermal voltage and the new k_{nr} after passivation, respectively.

This relation implies, V_{oc} increases by $\sim 4.6V_T$, when k_{nr} is reduced by an order of magnitude, and passivation has a larger impact at higher temperatures.

Table 2: Device performances and passivation strategies used in this work. Pero/HTL represents the interface between the perovskite and hole-transport layer.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Passivation strategies
Control average	1.141	23.2	70.9	18.8	None
Passivated1 average	1.153	23.3	71.8	19.4	Pero/HTL defect passivation
Passivated2 average	1.169	23.5	73.4	20.3	Pero/HTL defect passivation Pero/HTL band alignment

The measured qV_{oc} of one control FAMACs PSC and two interface-passivated FAMACs PSCs are shown in Fig. 3d and Fig. 3e. The device performances and passivation strategies are reported in Tab. 2. More details can be found in our previous work.¹⁹ Since qV_{oc} is typically smaller than μ_{PVK} caused by the limited charge selectivity of contacts, charge recombination at the contacts, and the energetic offset of majority carriers at the interfaces,^{20, 46-53} Fig. 3d and 3e cannot confirm that PLr reduces μ_{PVK} in our FAMACs PSCs. However, Fig. 3e indicates that neglecting PLr results in an overestimation of the effective k_{nr} . This also holds when extracting k_{nr} from the J - V curve. In actual PSCs, the J - V relation can be described by the following two-diode model:²³

$$J(V) = J_{ph} - J_{nr} - J_2 - \frac{V + Jr_s}{r_{sh}} \quad (16a)$$

$$J_{nr} = \left(e^{\frac{V+Jr_s}{2V_T}} - 1 \right) J_{nr}^0, \quad J_{nr}^0 = k_{nr} n_i q d \quad (16b)$$

$$J_2 = \left(e^{\frac{V+Jr_s}{V_T}} - 1 \right) J_2^0, \quad J_2^0 = (1 - \eta_{PLr}) k_2 n_i^2 q d \quad (16c)$$

where J_{nr} and J_2 are the current loss due to k_{nr} and k_2 , respectively; η_{PLr} and n_i are the PLr ratio and intrinsic carrier density determined by Eqn. 5 and Eqn. 14c, respectively. Eqn. 16 shows that the J - V curve can be represented by k_{nr} , k_2 , r_s , r_{sh} , and J_{ph} . Because n_i is small, J_{nr} and J_2 are negligible under J_{sc} condition. Hence, for simplicity we replace J_{ph} with J_{sc} :

$$J(V) = J_{sc} - J_{nr} - J_2 + \frac{V + Jr_s}{r_{sh}} \quad (17)$$

If using V_{oc} conditions (i.e. $J=0$ in Eqn. 17), J_{sc} cancels and we obtain a better fit, since the current mainly varies at high voltage:

$$J(V) = \left(e^{\frac{V_{oc}}{2V_T}} - e^{\frac{V+Jr_s}{2V_T}} \right) J_{nr}^0 + \left(e^{\frac{V_{oc}}{V_T}} - e^{\frac{V+Jr_s}{V_T}} \right) J_2^0 + \frac{V_{oc} - V - Jr_s}{r_{sh}} \quad (18)$$

Fixing k_2 at 2×10^{-10} cm³/s and using k_{nr} , r_s , r_{sh} as free parameters reproduces the experimentally-measured J - V curve well (see Fig. 3f). It is noteworthy that Eqn. 18 can only be used to fit data, it cannot be used to simulate the J - V relation using preset J_{nr} , J_2 , and r_{sh} , since V_{oc} depends on them. The fitting results are given in Tab. 3. k_{nr} decreases with passivation as expected. Again, neglecting PLr overestimates k_{nr} . The fitted values of r_s and r_{sh} are virtually unaffected by k_{nr} , indicating the current loss due to r_s and r_{sh} has a unique dependence on voltage. Following interface passivation, r_s decreases, while r_{sh} increases as expected. Since r_s is related to the interface contact properties (V loss in Fig. 3f) and r_{sh} is related to the interface leakage current (J loss in Fig. 3f), our fit indicates that the interface contact properties were improved by both passivation strategies, while the interface leakage current was further reduced by passivation due to better band alignment.

Table 3: Results of k_{nr} and r_s , r_{sh} extracted from the experimentally-measured J - V curves.

	k_2 (cm ³ /s, fixed)	k_{nr} (s ⁻¹)	r_s ($\Omega \cdot \text{cm}^2$)	r_{sh} ($\Omega \cdot \text{cm}^2$)	k_{nr} (s ⁻¹) from Fig. 3e
Control	2×10^{-10} PLr	$(4.942 \pm 0.010) \times 10^6$	3.51 ± 0.03	510.64 ± 17.08	$\sim 5 \times 10^6$
Passivated1	2×10^{-10} PLr	$(4.281 \pm 0.007) \times 10^6$	2.51 ± 0.02	512.05 ± 13.64	$\sim 4 \times 10^6$
Passivated2	2×10^{-10} PLr	$(3.020 \pm 0.004) \times 10^6$	2.57 ± 0.02	826.40 ± 30.71	$\sim 3 \times 10^6$
Passivated2	2×10^{-10} no PLr	$(4.367 \pm 0.006) \times 10^6$	2.58 ± 0.02	826.11 ± 30.70	$\sim 4 \times 10^6$

To summarize, we revealed the space-dependent photoluminescence reabsorption (PLr) and its relation to the external PL quantum efficiency in perovskite thin films by photon diffusion theory. Furthermore, we proposed a dimensionless solution of the PLr ratio, which can be used to account for the PLr effect on the carrier recombination dynamics. Our solution is supported by steady-state PL and time-resolved PL spectra. Knowing the effect of PLr, we successfully used time-resolved terahertz spectroscopy to determine the intrinsic carrier recombination rate, which is typically masked by PLr and surface recombination. Finally, yet importantly, we developed a model to quantify the PLr effect on the perovskite's QFLS. In conclusion, we revealed that PLr is detrimental to QFLS at high k_{nr} , while it increases QFLS when k_{nr} is below a critical limit of $\sim 7 \times 10^5 \text{ s}^{-1}$. By fitting the J - V curves, we demonstrated that neglecting PLr overestimates the effective k_{nr} , while it has no impact on the values of r_s and r_{sh} . We found that r_s decreases and r_{sh} increases with passivation, indicating that the interface contact properties are improved and interface current leakage is suppressed by passivation. Overall, our findings provide insight into how QFLS depends on PLr, a prerequisite for future improvements of perovskite materials and interfaces in devices.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Supplementary information (PDF)

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Author Contributions

M.W. performed the steady-state and transient optical spectroscopy techniques and data analysis. He conceived and developed the theoretical model and wrote the initial draft of the paper. K.W. prepared the perovskite thin film samples and devices and performed the photovoltaic performance characterization. Y.G. and J.K. assisted in the ultrafast time-resolved experiments. W.Y. helped to refine the theoretical model. S.D.W. and F.L. supervised the work and revised the manuscript. All authors contributed to refining the final version of the manuscript.

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Supplementary Information

Impact of photoluminescence reabsorption and surface passivation in metal-halide perovskite solar cells

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Section 1. Materials and solar cell device preparation

The 1.2M MA₃ (MA) perovskite precursor solution was prepared by mixing CH₃NH₃I and PbI₂ with a molar ratio of 1:1 dissolved in in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (4:1 by volume) and stirred overnight at room temperature in the N₂ filled glove box (<1 ppm of H₂O and O₂). The 1.2M precursor solution of FA_{0.81}MA_{0.14}CS_{0.05}PbI_{2.55}Br_{0.45} (FAMAPbCsIBr) was prepared as per literature [1] and kept overnight at 60 °C with stirring. The solar-cell devices were fabricated using SnO₂ thin-film procedure on patterned ITO-coated glass. Perovskite solutions were spin coated on top of the SnO₂ layer at 2000 rpm for 10s with an acceleration of 200 rpm/s. Chlorobenzene (0.1 ml) was dropped on the spinning substrate during the second spin-coating step at 10s before end of the procedure. The films were then annealed at 100 °C for 10 min. After cooling down to room temperature, the hole-transporting layer was then deposited on top of the perovskite film via spin-coating at 4000 rpm for 30s using a chlorobenzene of a 80 mg/ml solution of 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine) 9,9'-spirobifluorene (spiro-MeOTAD), with additives of lithium bis(trifluoromethanesulfonyl) imide and 4-*tert*-butylpyridine. Finally, 20 nm of gold and 80 nm of silver thick electrodes were deposited by thermal evaporation using an Angstrom evaporator. The current-density–voltage (*J–V*) curves were measured using a solar simulator (Newport, Oriel Class A, 91195A) with a source meter (Keithley 2420) at 100 mA/cm² illumination (AM 1.5G) and a calibrated Si-reference cell certificated by NREL. All the solar cells were masked during the *J–V* measurements in order to define the active area of about 0.1 cm².

Figure S1: Top view scanning electron microscope (SEM) images.

Figure S2: EQE and optical loss spectra of FAMACs solar cells.

Section 2. Photoluminescence (PL) and time-resolved PL spectroscopy

Steady-state PL spectra were measured with a HORIBA-fluoroMax-4 in 30° reflection geometry as shown in Fig. S3, which also shows the key parameters. For the PL spectra shown in the main text, each measurement required 30 seconds. Our time-resolved photoluminescence (TR-PL) spectroscopy setup uses a nanosecond laser operating at 532 nm with a repetition rate of 1 kHz as excitation source. The excitation fluence was kept at $\sim 2 \mu\text{J}/\text{cm}^2$ and the initial carrier density was $\sim 5 \times 10^{17} \text{ cm}^{-3}$.

Figure S3: Scheme showing the excitation and detection layout and measurements parameters of the steady-state photoluminescence measurements.

Figure S4: Simulated charge carrier redistribution in the direction (x) along the film thickness induced by diffusion and PLr under continuous illumination.

Carrier redistribution due to diffusion and PLr

Due to the photogenerated carriers' high mobility in perovskite materials, diffusion-induced carrier redistribution cannot be neglected in thin films. Based on the fit results of data from terahertz experiments (see Tab. 1 in the main article), we simulated the carrier distribution in perovskite films with $d=600$ nm and $d=6000$ nm (Fig. S4). Since PLr also introduces carrier redistribution, we also simulated the case of 100-sun illumination (Fig. S4). We find diffusion-induced carrier redistribution is significant in thin films, while PLr-induced carrier redistribution is negligible.

Figure S5: Time-evolution of PL spectra of (a) MA and (b) FAMACs perovskite thin films. The right panel shows normalized spectra.

Examination of light-soaking effect

As we used a continuous excitation source to measure the steady-state PL, light-induced peak shifts must be considered [2,3]. To check for light-induced peak shifts, we performed time-dependent experiments by measuring PL spectra subsequently for 30 times. Each measurements took 10 seconds (Fig. S5a and S5b). We observed that light-soaking neither resulted in any peak shift in our samples nor in any change of shape over time.

Section 3. Elliott fit of the absorption spectra

Elliott's model can be used to extract the exciton binding energy assuming Wannier-type excitonic absorption in addition to absorption by continuum states [4,5]:

$$\alpha(E) \cdot E \propto 2\sqrt{R_{ex}^3} \sum_j \frac{1}{j^3} \delta\left(E - E_g + \frac{R_{ex}}{j^2}\right) + \frac{\sqrt{R_{ex}}\theta(E - E_g)}{1 - \exp[-2\pi\sqrt{R_{ex}}/(E - E_g)]} \quad (S1)$$

Here R_{ex} , E_g , δ , and θ are the binding energy of excitons, the energy gap, the Dirac delta function, and step function, respectively. The first term accounts for the excitonic resonance, while the second term accounts for the continuum-state absorption. To account for thermal broadening, $\alpha(E)$ is convoluted with a Voigt distribution of width Γ (Gaussian) and γ (Lorentzian). Finally, we obtained $\Gamma \sim 23.9$ meV/25.7 meV, $\gamma \sim 5.6$ meV/9 meV, $\text{co}R_{ex} \sim 9.9$ meV / ~ 10.6 meV and $E_g \sim 1.64$ eV / ~ 1.659 eV for MA / FAMACs, respectively.

Section 4. Determination of PL reabsorption

Compared to the diameter of the pump laser (~ 500 μm in TR-PL, ~ 8 mm in steady-state PL and ~ 3 mm in terahertz experiments), the sample's thickness is significantly less, so that the excitation can be considered restricted in one dimension. Thus, the photon density γ is coupled to the carrier density n [6,7]:

$$\frac{\partial \gamma(x, t, \lambda)}{\partial t} = D_\lambda \frac{\partial^2 \gamma}{\partial x^2} + k_2 n(x, t)^2 g(\lambda) - \frac{c}{n_s} \alpha_\lambda \gamma \quad (S2)$$

Where D_λ is the photon diffusion/propagation coefficient that results from photon scattering/transport [7], c , n_s , α_λ are the speed of light, the refractive index of perovskite, and absorption coefficient of the perovskite layer, respectively. $R_{PL} = k_2 n(x, t)^2 g_\lambda$ is the intrinsic PL emission through bimolecular recombination, with $g(\lambda)$ the spectral Gauss distribution. The last term represents the photon depletion rate through PLr.

As long as the photons diffuse much faster than the charge carriers, which is the case in perovskite films, $n(x, t)$ can be considered t -independent in Eqn. S1 (instantaneous PLr approximation). Hence, we can rewrite Eqn. S1 as:

$$\begin{cases} \frac{\partial \gamma(x, t, \lambda)}{\partial t} = D_\lambda \frac{\partial^2 \gamma}{\partial x^2} - \frac{c}{n_s} \alpha_\lambda \gamma \\ \frac{\partial \gamma(x, 0, \lambda)}{\partial t} = k_2 n(x)^2 g(\lambda) \end{cases} \quad \text{Initial condition} \quad (S3)$$

As n is space dependent, we separate the sample into m slices of the same thickness Δx so that each slice can be considered as a flat source. For a Gaussian source located at slice i , applying Green's function solution to Eqn. S2, yields:

$$\gamma(x, t, \lambda) = \exp\left[-\frac{c}{n_s} \alpha_\lambda t\right] \int \frac{\exp\left[-\frac{(x - x_i)^2}{4D_\lambda t}\right]}{\sqrt{4\pi D_\lambda t}} \gamma(x_i, 0, \lambda) dx_i \quad (S4)$$

Where the exponential decay in the integration is due to photon scattering and absorption. The solution for t -independence can be obtained by integrating Eqn. S3 over time and applying the initial condition in Eqn. S2:

$$\gamma(x, \lambda) = \frac{k_2 n(x_i)^2 g_\lambda}{2} \frac{\Delta x}{\sqrt{D_\lambda c \alpha_\lambda / n_s}} e^{-\sqrt{c \alpha_\lambda / D_\lambda n_s} |x - x_i|} \quad (S5)$$

Where the denominator ‘2’ accounts for the two propagation directions of photons. By assuming the scattering length in perovskite is $\sim 20 \mu\text{m}$ [8], which is equivalent to a scattering coefficient of $\alpha_s = 500 \text{ cm}^{-1}$, we obtain $D_\lambda = c/n_s/(\alpha_\lambda + \alpha_s)$ [7]:

$$\gamma(x, \lambda) = \frac{k_2 n(x_i)^2 g_\lambda}{2} \frac{\sqrt{(\alpha_\lambda + \alpha_s)/\alpha_\lambda} \Delta x}{c/n_s} e^{-\sqrt{(\alpha_\lambda + \alpha_s)\alpha_\lambda} |x - x_i|} \quad (S6)$$

Neglecting the small scattering coefficient and considering the time-dependent $n(x, t)$, the PLr rate G_{PLr0} due to the PL emission of all slices can be expressed by:

$$G_{PLr0}(x, t, \lambda) = \frac{\alpha_\lambda g_\lambda}{2} \int_0^d k_2 n^2(y, t) e^{-\alpha_\lambda |x - y|} dy \quad (S7a)$$

$$\eta_{PLr0}(\lambda) = g_\lambda \left[1 - \frac{1 - e^{-\alpha_\lambda d}}{\alpha_\lambda d} \right] \text{ for constant } n \quad (S7b)$$

$$\eta_{PLr0} = 1 - \frac{1 - e^{-\alpha_{PL} d}}{\alpha_{PL} d} \text{ for linear } \alpha_\lambda \quad (S7c)$$

where η_{PLr0} is the PLr ratio. Eqn. S71 is similar to Lambert-Beer’s absorption law. When n is a constant, the PLr efficiency can be integrated over y and x (Eqn. S7b). Further simplification can be achieved, when α_λ changes linearly in the PL emission region.

Multireflection in the escape cone

It is worth noting that Eqn. S7 is derived by neglecting internal reflections. However, in case of strong internal reflection, image sources can be added [9]. For simplicity, we assume that all internal reflections are restricted in one dimension, that is, photons only have two diffusion directions, while they can enter different modes (Fig. S6). For convenience we set $f_1 = \cos 22^\circ \approx 0.92$ and $f_2 = \cos 30^\circ \approx 0.86$. Then the PLr rate due to multireflection of photons in the escape modes is:

$$\frac{(1 - f_1) r_1 r_2 \alpha_\lambda g_\lambda}{2(1 - r_1 r_2 e^{-2\alpha_\lambda d})} \int_0^d k_2 n^2(y, t) \left\{ \frac{e^{-\alpha_\lambda(2d - x + y)} + e^{-\alpha_\lambda(2d + x - y)}}{e^{-\alpha_\lambda(x + y)}/r_2 + e^{-\alpha_\lambda(2d - x - y)}/r_1} \right\} dy \quad (S8)$$

where $(1 - f_1)/2 \approx 4\%$ is the probability that photons are reflected multiple times in the upper and lower cones without escaping. $r_1 \sim 0.2$ and $r_2 \sim 0.07$ are the reflectivity at the front and back interface, respectively. As $(1 - f_1) r_1 r_2$ is very small, the PLr rate due to internal reflections in the escape cones can be neglected.

PLr due to leaky modes

For the leaky modes of photons reflected once by the front surface, the PLr rate G_{lek} is:

$$G_{lek}(x, t, \lambda) \approx \frac{|f_1 - f_2|}{2} \alpha_\lambda g_\lambda \int_0^d k_2 n^2(y) e^{-\alpha_\lambda(x+y)} dy \quad (S9a)$$

$$\eta_{lek}(\lambda) = |f_1 - f_2| \frac{g_\lambda (1 - e^{-\alpha_\lambda d})^2}{2 \alpha_\lambda d} \quad \text{for constant } n \quad (S9b)$$

$$\eta_{lek} = |f_1 - f_2| \frac{(1 - e^{-\alpha_{PL} d})^2}{2 \alpha_{PL} d} \quad \text{for linear } \alpha_\lambda \quad (S9c)$$

Where $f_1 - f_2 = (\cos 22^\circ - \cos 30^\circ)/2 \approx 3\%$ is the probability that photons are reflected into leaky modes. η_{lek} is the fraction of PLr of leaky modes.

(a) Escape modes ~11%

(b) Leaky modes ~3%

(c) Guided modes ~86%

Figure S6: (a) Schematic of escape modes of PL photons. The effective escape probability at the perovskite/quartz interface is estimated by $\theta_{c2} = \arcsin [1/\sqrt{n_{quartz}n_{pvk}}]$ to account for edge leaks. (b) Schematic of leaky modes and its image source. (c) Schematic of internal reflections in the guided modes and their image sources.

PLr due to guided modes

For the guided modes, we consider the minimum of f_1 and f_2 (here $f_2=86\%$) is the probability that photons are reflected into the guided modes. Since the guided modes are in the total internal reflection region, photons are trapped in the film until they are reabsorbed or escape from the edges. Guided modes also suffer from microcavity effects in thin films [10]. By adding a series of image sources to account for multiple reflections, the PLr rate provided by guided modes (G_{gd}) is:

$$G_{gd}(x, t, \lambda) \approx \min(f_1, f_2) \frac{f_{mc} \alpha_\lambda g_\lambda k_2}{1 - e^{-2\alpha_\lambda d}} \int_0^d n^2(y, t) \left\{ \cosh[\alpha_\lambda(x - y)] e^{-2\alpha_\lambda d} + \cosh[\alpha_\lambda(x + y - d)] e^{-\alpha_\lambda d} \right\} dy \quad (S10a)$$

$$\eta_{gd}(\lambda) \approx \min(f_1, f_2) f_{mc} g_\lambda \frac{1 - e^{-\alpha_\lambda d}}{\alpha_\lambda d} \quad \text{for constant } n \quad (S10b)$$

$$\eta_{gd} = \min(f_1, f_2) f_{mc} \frac{1 - e^{-\alpha_{PL} d}}{\alpha_{PL} d} \quad \text{for linear } \alpha_\lambda \quad (S10c)$$

where η_{gd} is PLr efficiency of the guided modes. f_{mc} in Eqn. S10 is a coefficient accounting for the microcavity effect. According to the cavity order function [10]:

$$m_c \approx 2n_s d / \lambda, \quad m_c \leq 2n_s^2 \quad (S11)$$

When $m_c=2, 4, 6, \dots$, the total escape probability in the escape cones is doubled in a close-mirror approximation; n_s is material's refractive index. For simplicity, we model f_{mc} by assuming photons in the guided modes can be coupled out with a probability of $1/2n_s^2$ when $m_c=2, 4, 6, \dots$:

$$f_{mc} \approx 1 - \max(f_1, f_2) \frac{1}{2n_s^2} \cos^2\left(\frac{\pi m_c}{2}\right) \quad (S12)$$

Figure S7: Schematic of carrier and photon equilibrium state under continuum illumination in the presence and absence of PLr. η_{ext} can overcome the outcoupling limit (Eqn. S13) when n_{PLr} is large enough.

Modeling of outcoupling limit

The outcoupling limit (η_{oc}) is determined by escape cones and the microcavity effect:

$$\eta_{oc}(\lambda) = [1 - \max(f_1, f_2)] + |f_1 - f_2| + \min(f_1, f_2) \cdot (1 - f_{mc}) \quad (S13)$$

where the term with $\max(f_1, f_2)$, $|f_1 - f_2|$ and $\min(f_1, f_2)(1 - f_{mc})$ respectively account for the contribution of escape cones, leaky modes, and microcavity effects. All of the uncoupled photons are in guided modes. They can diffuse laterally and finally contribute to the nonradiative loss at other places where the internal PLQE is low (Fig. S7). In the case of the radiative limit, that is $\eta_{int}=1$, theoretically the uncoupled photons will be trapped in the material forever. However, PLr is always present in real materials, thus $\eta_{ext}=1$ in the radiative limit.

Modeling of internal PL spectra for bulk excitation

By adding image sources, and in the case that n is space-independent, the external PL flux in the presence of the PLr effect at the front surface is:

$$PL_{ext}(\lambda) \cong \frac{k_2 n^2 g_\lambda}{2} \int_0^d \{[(1 - f_1) + f_2(1 - f_{mc})] e^{-\alpha_\lambda y}\} dy$$

$$= \frac{k_2 n^2 g_\lambda}{2} [(1 - f_1) + f_2(1 - f_{mc})] \frac{1 - e^{-\alpha_\lambda d}}{\alpha_\lambda} \quad (S14)$$

The external PL flux in the absence of the PLr effect at the front surface is:

$$PL_{ext0}(\lambda) \cong \frac{k_2 n^2 g_\lambda d}{2} [(1 - f_1) + f_2(1 - f_{mc})] \quad (S15)$$

Hence, PL_{ext0} can be calculated from PL_{ext} by Eqn.14 and Eqn. 15. We note that the equations above ignore the change of carrier density due to PLr, so the calculated PL_{ext0} should deviate from the real value. However, since the distribution of carrier density changes is almost space independent in the case of bulk-excited PL, these equations are sufficient to check the PLr-induced redshift of PL spectra obtained by bulk excitation.

Section 5. Time-resolved terahertz spectroscopy setup (TRTS)

Our TRTS setup uses a commercial Ti:sapphire amplifier operating at 800 nm with a repetition rate of 3 kHz as laser source. Its pulse width (FWHM) is compressed to ~120 fs. The THz emitter and detector are two 1 mm thick <110> oriented zinc telluride (ZnTe) crystals. All the THz related optics were placed in a closed chamber, which was continuously purged with pure nitrogen gas. Perovskite samples were excited by 550 nm laser pulses obtained from a TOPAS pumped by the fundamental of the fs amplifier. THz probe pulses and 550 nm pump pulses were chopped at 499 Hz and 3×499 Hz by two optical choppers, respectively, to collect dark and excited state signals with one Lock-in Amplifier by adjusting its harmonic reference. A stepper motor mounted to a circular ND filter was used to change the pump fluence in the fluence dependent experiments.

Section 6. Global fitting procedure for TRTS kinetics

Following photoexcitation and carrier creation, the THz electrical field transmitted through the perovskite sample changes from E_0 to $E(t)$. We recorded the time dependent change $\Delta E(t)/E_0 = (E(t) - E_0)/E_0$ at the peak of E_0 as TRTS kinetics. Assuming that the carrier mobility does not change when carriers recombine (see the main article), TRTS kinetics mainly reflect the density of free carriers, following the general rate equation, as mentioned in the main article:

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - k_1 n - k_2 n^2 - k_3 n^3 + G_0 + G_{PLr} \quad (S16)$$

Here, D is the ambipolar diffusion coefficient for both electrons and holes, given by the Einstein relation $D = \mu_a k_B T / q$, where μ_a , k_B , T , and q are the ambipolar mobility, Boltzmann constant, absolute temperature, and unit charge, respectively; $G_{PLr} = G_{PLr0} + G_{lek} + G_{gd}$ is the carrier generation rate due to PLr (Eqn. S7, S9, S10); G_0 is the generation rate of carriers by photoexcitation, which obeys Lambert-Beer's law; As our pump laser pulse is ultrashort, G_0 can be described by:

$$n(x, 0) = \varphi \cdot F_{ph} \cdot \alpha(\lambda) e^{-\alpha(\lambda)x} \quad (S17)$$

Here, φ is the quantum yield of free carrier generation, and F is the photon fluence calculated obtained by deducting the surface-reflected photons from the total incident photons:

$$F_{ph} = \frac{P(1 - R_{\text{pump}})}{1500 \cdot \pi \cdot (D_{\text{FWHM}}/2)^2 \cdot E_{ph}}, \quad E_{ph} = \frac{hc}{\lambda} \quad (\text{S18})$$

Where P is the pump power. The number 1500 (s^{-1}) denotes the number of pulses that pass the optical chopper in one second. D_{FWHM} represents the diameter of our pump beam determined as FWHM in power, calculated from the ratio of the maximum power transmitted through a 1-mm pinhole to its original power:

$$\text{FWHM} = \sqrt{-\frac{\ln 2}{\ln(1 - T_{\text{max}})}} \text{ mm} \quad (\text{S19})$$

Here, the diameter of our pump beam in FWHM is ~ 3.05 mm as calculated from the measured $T_{\text{max}} \sim 7.2\%$.

To solve Eqn. S16, initial conditions and boundary conditions are introduced. The initial condition is shown in Eqn. S17, $\varphi=1$. The boundary conditions are the same as introduced in the main article:

$$D \frac{\partial n(0, t)}{\partial t} = S_0 \cdot n(0, t) \quad D \frac{\partial n(d, t)}{\partial t} = -S_d \cdot n(d, t) \quad (\text{S20})$$

Where S_0 and S_d are the surface recombination velocities at the front and back surface, respectively; d is the thickness of the film.

If the quantum yield of free carriers, bulk and surface recombination rates, and carrier mobility are fluence independent, we can perform a global fit of the data using Eqn. S7, S9, S10, S16, S17 and S20.

Determination of $\mu_n + \mu_p$

Determination of $\mu_n + \mu_p$: When the thickness of our perovskite sample is much smaller than the THz wavelength, then the value of $\mu_n + \mu_p$ right after photoexcitation can be estimated from the amplitude of the TRTS kinetics [11]:

$$(\mu_n + \mu_p) \cdot q \int_0^d n(x, 0) dx = -\varepsilon_0 c(n_A + n_B) \cdot \max\left(\frac{\Delta E(t)}{E_0}\right) \quad (\text{S21})$$

Where $n_A=2.13$ and $n_B=1$ are the refractive indices of z-cut quartz and nitrogen gas, respectively. As the maximum values of TRTS kinetics have nonlinear fluence-dependence at high fluence, $\mu_n + \mu_p$ calculated from high fluence measurements deviates from the value calculated from low fluence (see Figure 2b in the main article) measurements. As a result, the quantum yield of free carriers or the carrier mobility is not fluence independent at high fluence. In order to obtain a global fit using the assumption of fluence-independent quantum yield and mobility, all the F_{ph} at high fluence were calibrated by fixing the $\mu_n + \mu_p$ at its value calculated from the low fluence data ($< 30 \mu\text{J}/\text{cm}^2$).

The lower and upper limit of the radiative recombination rate

As the recombination caused by k_1 does not change at different carrier density, the power-dependent behavior in the TRTS kinetics must originate from processes linked to k_2 . The onset carrier density can be defined as $n_{pd} = k_{1eff} / (k_2)_{app}$, where $(k_2)_{app}$ is the apparent bimolecular recombination rate related to k_2 by $(k_2)_{app} = (1 - \eta_{PLr})k_2$ (this is valid throughout the carrier decay, because η_{PLr} is independent of the carrier density and diffusion for exponentially-distributed carriers, see main article). Since power-dependent decays are observed above $n_{pd} \sim 1 \times 10^{18} \text{ cm}^{-3}$ for MA and $n_{pd} \sim 2 \times 10^{18} \text{ cm}^{-3}$ for FAMACs in our experiments (Figure S8), the fitted k_2 should satisfy:

$$k_{1eff}n_{pd} \leq (1 - \eta_{PLr})k_2n_{pd}^2 \quad (S22)$$

which yields lower limits of k_2 of $6.09 \times 10^{-11} \text{ cm}^3/\text{s}$ and $5.22 \times 10^{-11} \text{ cm}^3/\text{s}$ for MA and FAMACs, respectively.

Figure S8: Power-dependent THz signal dynamics for MA and FAMACs samples, respectively.

The fitted k_2 can be evaluated by determining the number of reabsorbed photons. Here we start by using the diffusion rate:

$$R_{diff} = D \frac{\partial^2 n(x)}{\partial x^2} = D \cdot \alpha_{pump}^2 n_0 e^{-\alpha_{pump} x} \quad (S23)$$

PLr can also lead to carrier renormalization (Fig. 1c in the main article). The ‘diffusion rate’ induced by PLr is:

$$R_{PLr} = \eta_{PLr} k_2 n^2(x) = \frac{\eta_{PLr} k_2 n_0}{4\alpha_{pump}^2} \cdot (2\alpha_{pump})^2 n_0 e^{-2\alpha_{pump} x} \quad (S24)$$

Consequently, the effective diffusion coefficient of PLr is:

$$D_{PLr} = \frac{\eta_{PLr} k_2 n_0}{4\alpha_{pump}^2} \quad (S25)$$

We find D_{PLr}/D is proportional to the carrier density. If PLr significantly contributes to the carrier mobility, then the measured mobility should increase with fluence. Here we expect $D_{PLr} < 0.2D$ for the highest n_0 ($7.6 \times 10^{18} \text{ cm}^{-3}$), because the measured carrier mobility has no obvious fluence-dependent behavior (Fig. 2b in the main article), thereby providing an upper limit of k_2 of $2.55 \times 10^{-10} \text{ cm}^3/\text{s}$ and $1.93 \times 10^{-10} \text{ cm}^3/\text{s}$ for MA and FAMACs samples, respectively.

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