Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Quantitative Analysis of the Transient Photoluminescence of $CH_3NH_3PbI_3/PC_{61}BM$ Heterojunctions by Numerical Simulations

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Table S1. Parameter used in simulation. Taken from[1] and measured in our group. If a parameter is stated only for one material the parameter has been assumed to be the same in perovskite (bulk) and $PC_{61}BM$ (quencher).

parameter	value
bandgap perovskite $E_{\mathrm{g,b}}$	1.6 eV
bandgap $PC_{61}BM$ $E_{\mathrm{g,q}}$	1.75 eV
electron affinity perovskite $E_{\mathrm{EA,b}}$	4 eV
electron affinity $PC_{61}BM$ $E_{\mathrm{EA,q}}$	4.2 eV
thickness perovskite d_{b}	300 nm
thickness $PC_{61}BM$ d_{q}	100 nm
relative permittivity perovskite $\varepsilon_{\mathrm{r,b}}$	30
relative permittivity $PC_{61}BM$ $\varepsilon_{\mathrm{r,q}}$	3.9
radiative recombination coefficient k_{rad}	4.78×10^{-11} $\mathrm{cm}^3 s^{-1}$
Auger recombination coefficient C_{Aug}	4.4×10^{-29} $\mathrm{cm}^6 s^{-1}$
SRH lifetime electrons $\tau_{\mathrm{SRH,n}}$	511 ns
SRH lifetime holes $\tau_{\mathrm{SRH,h}}$	871 ns
doping density $N_{\mathrm{D/A}}$	undoped
effective density of states N_{V}	2.22×10^{18} cm^3
effective density of states N_{C}	2.22×10^{18} cm^3
mobility μ	20 $\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$
temperature T	300 K
laser pulse width	1 ns
laser power	1-10000 $\mathrm{W/cm}^2$
laser wavelength λ	496 nm

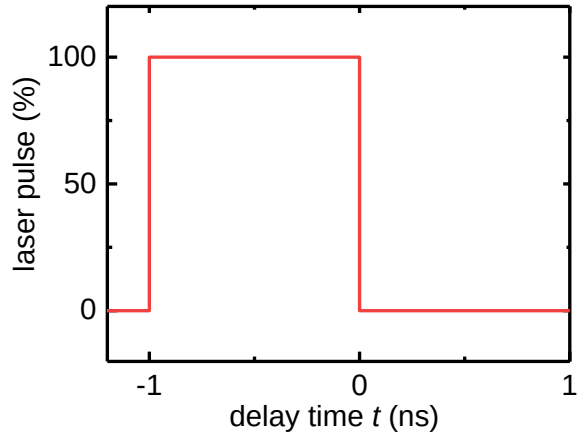

Figure S1. Shape of the laser pulse used in the simulations. Delay time is always defined as the time passed since the end of the laser pulse.

Calculating the reabsorption

The density of photons emitted at each location is given by the radiative recombination rate $R_{\mathrm{rad}}(x)$ The photon density per photon energy $\Lambda(x,E)$ can be calculated with the Equation[2]

$$\Lambda(x,E) = \frac{R_{\mathrm{rad}}(x)\alpha(E)n_{\mathrm{r}}^2(E)\phi_{\mathrm{BB}}(E)}{\int_0^\infty \alpha(E)n_{\mathrm{r}}^2(E)\phi_{\mathrm{BB}}(E)dE} \quad \text{(S1)}$$

with α the absorption coefficient, n_{r} the refractive index and ϕ_{BB} the black body spectrum.

The photon flux per photon energy at the front interface is calculated from $\Lambda(x,E)$ by integrating over the thickness of the perovskite layer W and assuming Lambert-Beer absorption.

$$\phi(E) = \int_0^W \Lambda(x,E)\mathrm{e}^{-\alpha(E)x}dx \quad \text{(S2)}$$

The PL photon flux is then calculated by integrating over energy and normalizing it.

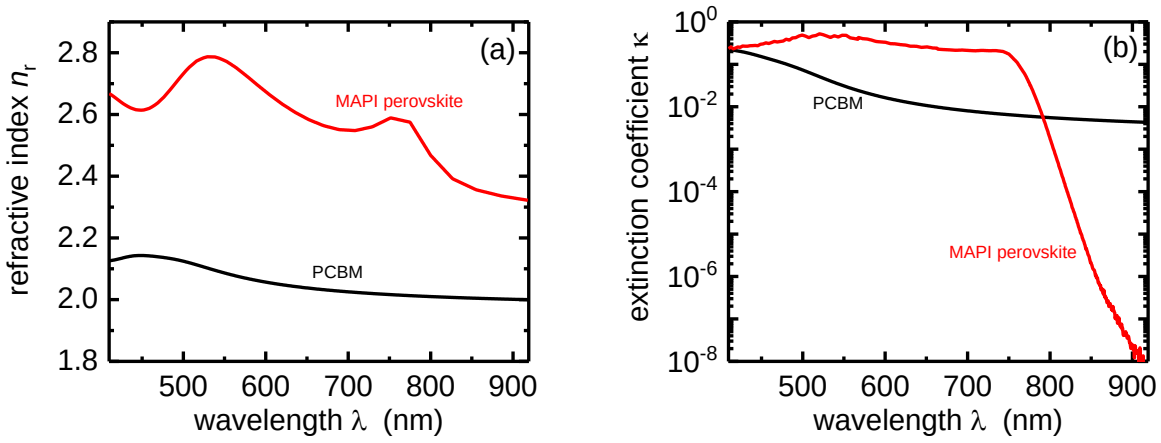

Figure S2. Refractive index n and extinction coefficient κ used for reabsorption calculations and in the simulations for the calculation of generation via the transfer matrix method. We the obtained optical data by modeling transmission and reflection data, gained by UV/VIS spectrometry, with the software SCOUT.

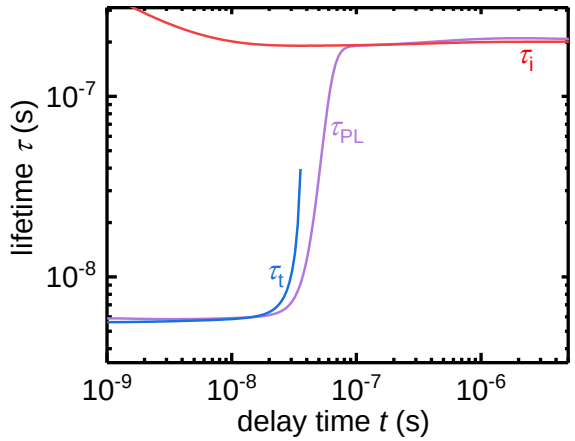

Figure S3. Lifetimes for the case S = 100 cm/s and E_L = 1 nJ/cm². The differential lifetime τ_{PL} is displayed in Figure 2a as well. We calculated the transfer lifetime τ_t with the equation $\tau_t \approx \overline{n_b} d_b q / J_T$ here is $\overline{n_b}$ the average electron density in the bulk (perovskite) and q the elemental charge and the transfer current J_T can be calculated with Equation 1. The interfacial-recombination lifetime τ_i has been calculated with the equation $\tau_i \approx 2\,\overline{p_b} d_b / R_{int}$ here is $\overline{p_b}$ the average hole density in the bulk R_{int} is the interface-recombination rate (Equation 2). τ_t fits very well to τ_{PL} at short times where transfer dominates and τ_i fits well at longer times where the interfacial recombination dominates.

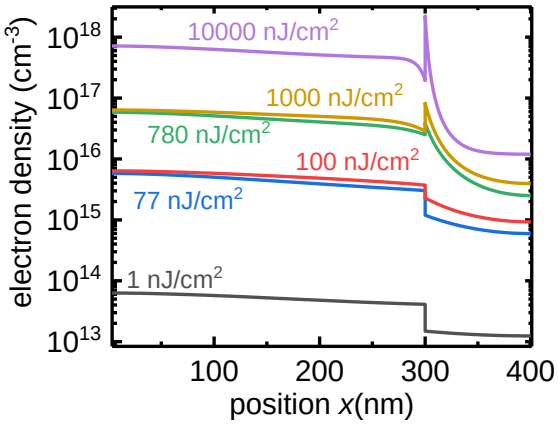

Figure S4. Electron density as a function of laser flux shortly (t = 68 ps) after the laser pulse. 100 nJ/cm² for the high E_L case in Figure 1c. 1 nJ/cm² and 1000 nJ/cm² for the cases in Figure 2b and 2d, respectively. 77 nJ/cm² , 780 nJ/cm² and 10000 nJ/cm² for the same case as in Figure 3c and 3d. The electrons can transfer during the laser pulse (-1 ns<t<0 ns). and therefore accumulation can be seen at high fluences already at short times.

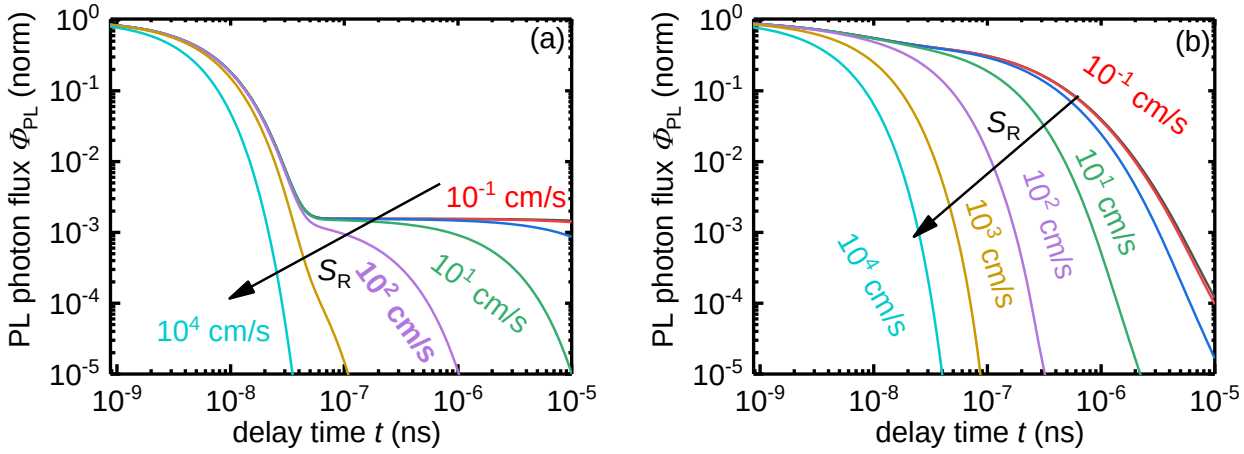

Figure S5. PL photon flux for varied interfacial recombination velocities and two laser fluences (a) 1 nJ/cm² (b) 1000 nJ/cm². We calculated the differential lifetimes in Figure 2a and 2c are from the data displayed here.

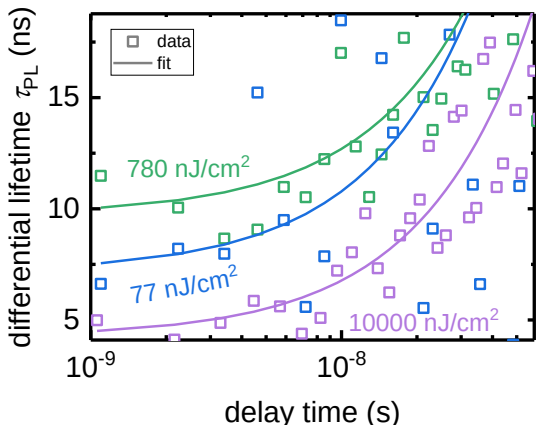

Figure S6. Differential lifetime calculated with Equation 4 from the data plotted in Figure 3a We fitted the arbitrary fit function $\tau_{\mathrm{PL,fit}}(t) = (at + b)/(t + c)$ to the differential lifetime. We calculated the fit in Figure 3a from $\tau_{\mathrm{PL,fit}}(t)$ with the inverse of Equation 4: $\Phi_{\mathrm{PL,fit}}(t) = \exp\left(\int_0^t -1/\tau_{\mathrm{PL,fit}}\, dt\right)$.

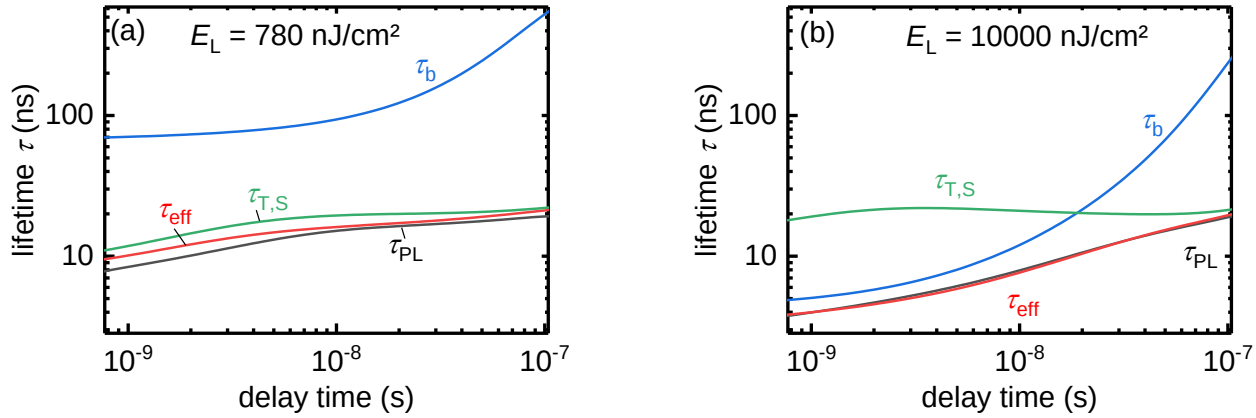

Figure S7. Influence of higher order recombination on PL transient at high laser fluence. The differential lifetime τ_{PL} in (a) and (b) are the same as in Figure 3d for the 780nJ/cm² and the 10000nJ/cm² case, respectively. In the 780nJ/cm² case the differential lifetime is dominated by the transfer/interfacial lifetime $\tau_{\mathrm{T,S}}$ while in the 10000 nJ/cm² case both the bulk lifetime and the transfer have an impact on the resulting differential lifetime. Note that the $\tau_{\mathrm{T,S}}$ The bulk lifetime τ_{b} is calculated with Equation S3-S6 from the bulk recombination rate R_{b}. The transfer/interfacial lifetime $\tau_{\mathrm{T,S}}$ is calculated with Equation S7-S9.

$$R_{\mathrm{b}} = \frac{\overline{n_{\mathrm{b}}}\,\overline{p_{\mathrm{b}}}}{\overline{n_{\mathrm{b}}}\tau_{\mathrm{SRH,p}} + \overline{p_{\mathrm{b}}}\tau_{\mathrm{SRH,n}}} + k_{\mathrm{rec}}\overline{n_{\mathrm{b}}}\,\overline{p_{\mathrm{b}}} + C_{\mathrm{Aug}}(\overline{n_{\mathrm{b}}} + \overline{p_{\mathrm{b}}})\overline{n_{\mathrm{b}}}\,\overline{p_{\mathrm{b}}} \quad \text{(S3)}$$

with $\overline{n_{\mathrm{b}}}$ and $\overline{p_{\mathrm{b}}}$ the average charge carrier density in the bulk. We estimate an equivalent lifetime for electrons and holes in the bulk with

$$\tau_{\mathrm{b,n}} \approx \overline{n_{\mathrm{b}}} d_{\mathrm{b}}/R_{\mathrm{b}} \quad \text{(S4)}$$

$$\tau_{\mathrm{b,p}} \approx \overline{p_{\mathrm{b}}} d_{\mathrm{b}}/R_{\mathrm{b}} \quad \text{(S5)}$$

and calculate the effective bulk lifetime with

$$\frac{1}{\tau_{\mathrm{b}}} = \frac{1}{\tau_{\mathrm{b,n}}} + \frac{1}{\tau_{\mathrm{b,p}}}. \quad \text{(S6)}$$

Analogous we calculate from the transfer currents $J_{\mathrm{T,n}}$ and $J_{\mathrm{T,p}}$ (for holes) from the interfacial recombination velocity a the transfer/surface lifetime $\tau_{\mathrm{T,S}}$

$$\tau_{\mathrm{T,S,n}} = q\,\overline{n_{\mathrm{b}}} d_{\mathrm{b}}/(-J_{\mathrm{T,n}}) \quad \text{(S7)}$$

$$\tau_{\mathrm{T,S,p}} = \overline{p_{\mathrm{b}}} d_{\mathrm{b}}/(J_{\mathrm{T,p}}/q + R_S) \quad \text{(S8)}$$

$$\frac{1}{\tau_{\mathrm{T,S}}} = \frac{1}{\tau_{\mathrm{T,S,n}}} + \frac{1}{\tau_{\mathrm{T,S,p}}} \quad \text{(S9)}$$

We calculate the plotted effective lifetime from the bulk and the transfer/interfacial lifetime with

$$\frac{1}{\tau_{\mathrm{eff}}} = \frac{1}{\tau_{\mathrm{b}}} + \frac{1}{\tau_{\mathrm{S,T}}}. \quad \text{(S10)}$$

Calculating the error

We calculated the error for Figure 4 with the equation

$$\Sigma_{\mathrm{err}} = \sum_{i=1}^{m} \left(\ln\left(\tau_{\mathrm{PL,v},i}\right) - \ln\left(\tau_{\mathrm{PL,r},i}\right)\right)^2 \quad \text{(S11)}$$

with m the number of simulation points, $\tau_{\mathrm{PL,v},i}$ the differential lifetime at a certain measurement point calculated from the varied parameters and $\tau_{\mathrm{PL,r},i}$ the reference differential lifetime the same measurement point.

References for Supporting Information

1 F. Staub, H. Hempel, J.-C. Hebig, J. Mock, U. W. Paetzold, U. Rau, T. Unold, T. Kirchartz, *Phys. Rev. Appl.* 2016, **6**, 44017.

2 T. Kirchartz, F. Staub, U. Rau, *ACS Energy Lett.* 2016, **1**, 731.