Supplementary Material - Quantifying photon recycling in solar cells and light emitting diodes: absorption and emission are always key

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Supplementary Note 1 – definition of all terms used in paper

Symbol	Definition
A	The area of the front of the semiconductor slab (m^2)
a	First order loss rate (generally interpreted as Shockley-Reed-Hall loss rate, see SM note 3) (s^{-1})
$a(E)$	Absorptance, fraction of diffuse external light absorbed by a material
$a_{direct}(E)$	Direct absorptance, fraction of solar radiation absorbed when sun at normal incidence to solar cell
$a_{front}(E)$	Diffuse absorptance for light incident on the front side of the slab
$a_{back}(E)$	Diffuse absorptance for light incident on the rear side of the slab
B	A constant (see SM note 5)
c	Third order loss rate (generally interpreted as Auger loss, see SM note 3)
E	Energy (J)
E_g	Bandgap of a solar cell (J)
$ELQE_{ext}$	The external electroluminescence quantum efficiency
f_p	Fraction of generated light parasitically absorbed
G	Total excitation generation rate at a point in a material ($cm^{-3}s^{-1}$)
G_{ext}	Excitation generation rate due to external illumination ($cm^{-3}s^{-1}$)
i	Dummy index of summation (corresponding to all processes in an arbitrary system)
$J(V)$	Current density in a solar cell (Am^{-2}) (see SM note 3)
J_{sc}	Short circuit current (Am^{-2}) (see SM note 3)
J_0	Recombination current (Am^{-2}) (see SM note 3)
k	A non-dimensional constant between 0 and 1
k_B	Boltzmann constant (JK^{-1})
k_1	First order recombination term (Am^{-2}) (see SM note 3)
k_3	Third order recombination term (Am^{-2}) (see SM note 3)
L	Fraction of initial excitations which escape the material (see SM note 2)
L_x	Probability an initial excitation undergoes x recycling events before escaping the slab
M	Arbitrary number of initial excitations (see SM note 2)
N	Average number of photon recycling events per externally absorbed photon
N_{obs}	Number of photon recycling events undergone by an escaping photon
$N_{\gamma,out}$	Number of photons emitted per unit area on the surface of a material
$n(E)$	Refractive index of a material

n	Excited electron concentration within a material (cm^{-3})
n_i	Intrinsic electron concentration within a material (cm^{-3})
$PLQE_{ext}$	The external photoluminescence quantum efficiency
$PLQE_{int}$	The internal photoluminescence quantum efficiency
p	The probability of a photon recycling event
p_i	Probability for arbitrary process i
q	Charge of an electron (C)
R_{nr}	Non-radiative recombination rate ($cm^{-3}s^{-1}$)
R_r	Radiative recombination rate ($cm^{-3}s^{-1}$)
T	Temperature (K)
t	Sample thickness (m)
V	Voltage (V)
V_{oc}	Open circuit voltage (V)
X_i	The outcome of arbitrary process i
$\langle X \rangle$	The average outcome of all process for all possible i
$\alpha(E)$	Absorption coefficient (m^{-1})
δ	A small energy, much less than the range of energy in AM1.5 (E)
$\epsilon(E)$	The emissivity of a sample
Θ	Photopic luminosity function
θ_c	Critical angle for a material, $\sin(\theta) = \frac{1}{n}$
θ_0	Polar angle through which solar cell interacts with it surroundings (see SM note 4)
$\tilde{\theta}$	$\sin(\tilde{\theta}) = \dfrac{\sin(\theta_{out})}{n(E)}$
θ_{out}	The polar angle of interaction with the surroundings. In our simulations either 90° or 2.5° in our simulations
$\eta_{esc}(E)$	The escape probability at energy E
$\bar{\eta}_{esc}$	The energy averaged escape probability
μ	Chemical potential (E)
$\Phi_{bb}(E)$	Black body flux per unit area per unit solid angle ($m^{-2}J^{-1}$)
$\Phi_{AM1.5}(E)$	AM1.5 solar flux per unit area ($m^{-2}J^{-1}$)

Supplementary Note 2 – derivation of the escape probability

According to the van Roosbroeck-Shockley relation, the number of photons generated per unit volume per unit energy within a material in the dark at energy E is [1,2]

$$4\pi n(E)^2 \alpha(E) \Phi_{bb}(E).$$

Here $n(E)$ is the local refractive index of the slab, $\alpha(E)$ its absorption coefficient and $\Phi_{bb}(E)$ the photon flux emitted by the surface of a black body into air (per unit area, per unit solid angle, per unit energy). With non-zero chemical potential, μ, the number of photons emitted is multiplied by $e^{\frac{\mu}{k_B T}}$, where $k_B T$ is the thermal energy. For a material with surface area A emitting $N_{\gamma,out}(E)$ photons per unit area per energy interval to the surroundings (i.e. the photons escaping the material), we can define the probability of a photon of energy E escaping as

$$\eta_{esc}(E) = \frac{No.\,of\ escaping\ photons\ of\ energy\ E}{No.\,of\ photons\ of\ energy\ E\ generated} = \frac{A N_{\gamma,out}(E)}{4\pi n(E)^2 \alpha(E) \Phi_{bb}(E) A t e^{\frac{\mu}{k_B T}}},$$

where t is the thickness of the absorber layer. We can also define the number of photons emitted relative to a black body surface, the (angle-averaged) emissivity, as:

$$\epsilon(E) = \frac{No.\,of\ escaping\ photons\ of\ energy\ E}{No.\,of\ escaping\ photons\ from\ black\ body\ at\ energy\ E} = \frac{A N_{\gamma,out}(E)}{\pi A \Phi_{bb}(E) e^{\frac{\mu}{k_B T}}}.$$

Combining the equations for $\eta_{esc}(E)$, $\epsilon(E)$ and noting $a(E) = \epsilon(E)$ leads to equation 1 in the main text.

A final note is that in the main text we give

$$\bar{\eta}_{esc} = \frac{\int \pi a(E) \Phi_{bb}(E) dE}{t \int 4\pi n(E)^2 \alpha(E) \Phi_{bb}(E) dE}.$$

If parasitic absorption is of importance then f_p, the fraction of generated light lost to parasitic absorption, is added to the right-hand side.

Supplementary Note 3 – modelling solar cell efficiency

The extracted current density from a solar cell with short circuit current density J_{sc} is given by

$$J(V) = J_{sc} - qt \times (\bar{\eta}_{esc}R_r + R_{nr})$$

assuming a uniform excitation density. For a halide perovskite we suggest that charges decay according to first, second and third order rates. These decay processes are generally interpreted to be trap-assisted non-radiative recombination, radiative bimolecular recombination and Auger recombination, respectively. Mathematically, $R_r = 4\pi n(E)^2 \alpha(E) \Phi_{bb}(E)(n^2 - n_i^2)$ and $R_{nr} = a(n - n_i) + c(n^3 - n_i^3)$. Here n is the charge density, n_i the background charge density, a the charge trapping rate and c the Auger recombination rate. The same absorption coefficient, refractive index, intrinsic electron concentration and Auger recombination rate are used as in previous descriptions [3]. Intrinsic electron concentration and Auger recombination coefficient are independent of thickness, charge-trapping rate and absorption. We used experimental absorption coefficients and refractive indices to calculate different absorptances within the manuscript. In addition, we assume that in the case of an intrinsic semiconductor $n = n_i e^{\frac{qV}{2k_BT}}$ where the chemical potential is equal to the voltage qV. This leads to

$$J(V) = J_{sc} - k_1 \left(e^{\frac{qV}{2k_BT}} - 1 \right) - J_0 \left(e^{\frac{qV}{k_BT}} - 1 \right) - k_3 \left(e^{\frac{3qV}{2k_BT}} - 1 \right),$$

$$J_{sc} = q \int \Phi_{AM1.5}(E) a_{direct}(E) dE \ ,$$

$$J_0 = q\pi \int \Phi_{bb}(E) a(E) dE \ .$$

Here $\Phi_{AM1.5}$ is the AM1.5 flux per unit area per unit energy and $a_{direct}(E)$ the fraction of this flux absorbed by the solar cell. We have used the definition of the escape probability given by equation 2 in the main text to obtain the equation for the recombination current J_0. Here $k_1 = qtan_i$ and $k_3 = qtcn_i^3$.

For a solar cell the PLQE is

$$PLQE_{ext}(V) = \frac{J_0 \left(e^{\frac{qV}{k_BT}} - 1 \right)}{J_{sc}}.$$

We note that this definition of PLQE is different to some previous reports [3,4], but we use this definition because it corresponds precisely to what external PLQE would be measured at any applied voltage when there is net charge extraction. We further explore the PLQE as a function of voltage in Figure S7, where we show the external $PLQE$ as a function of thickness for both

open-circuit and maximum power point. Within our definition, at maximum power point the external $PLQE$ is more than an order of magnitude lower than at open-circuit.

Using our three absorptance models (supplementary table 1) we calculate $\bar{\eta}_{esc}$ as a function of cell thickness in Figure S6. In the Direct case the escape probability is less than 10 % at all thicknesses due to the strong confinement effect of a flat cell surface. By contrast, Randomized and Maximal have much higher escape probabilities at low thicknesses (< 200 nm), but these escape probabilities rapidly reduce to below 30 % as the thickness is increased towards values resembling a realistic solar cell (~500 nm), due to photon reabsorption. We note that for all absorptance models we have accounted for changes in both short circuit and recombination currents.

Supplementary Note 4 – example of open circuit voltage increasing while solar cell efficiency is reduced

In the main text (Figure 3b) we show an increase in the open circuit voltage (V_{oc}) can reduce solar cell efficiency if this increase is because of a reduction in absorptance at the band-edge. To give a detailed example of this phenomenon, we present a Shockley-Queisser model (which has maximum possible efficiency for a solar cell) and reduce the absorptance at the band edge. We emphasize that V_{oc} will always increase for a reduction in the number of charge traps. In this model there is only radiative bimolecular recombination so

$$J(V) = J_{sc} - J_0 \left(e^{\frac{qV}{k_B T}} - 1 \right),$$

and

$$a_{direct}(E) = a(E) = \begin{cases} 0 \ for \ E < E_g \\ 1 \ for \ E > E_g \end{cases}$$

where E_g is the bandgap of the solar cell. The open circuit voltage is given by

$$V_{oc} = \frac{k_B T}{q} \ln\left(\frac{J_{sc}}{J_0} + 1\right).$$

We now consider the case where there is a reduction in absorption near the bandgap,

$$a_{direct}(E) = a(E) = \begin{cases} 0 \ for \ E < E_g \\ k \ for \ E_g < E < E_g + \delta \\ 1 \ for \ E > E_g + \delta. \end{cases}$$

Here k is a constant less than 1 and δ is an energy much less than the range of the solar spectrum. There will be an increase in V_{oc} with this model if $\frac{\tilde{J}_{sc}}{\tilde{J}_0} > \frac{J_{sc}}{J_0}$, where the 'tilde' corresponds to the case with reduced absorption near the bandgap. We note that $\Phi_{bb} = BE^2 e^{-\frac{E}{k_B T}}$, where B is a constant. Re-arranging the above inequality we obtain

$$\frac{\int_{E_g}^{E_g+\delta} E^2 e^{-\frac{E}{k_B T}} dE}{\int_{E_g}^{\infty} E^2 e^{-\frac{E}{k_B T}} dE} > \frac{\int_{E_g}^{E_g+\delta} \Phi_{AM1.5}(E) dE}{\int_{E_g}^{\infty} \Phi_{AM1.5}(E) dE}$$

which if true corresponds to an increase in V_{oc} beyond that in the Shockley-Queisser limit. If our bandgap is much larger than the thermal energy, $k_B T$ (as it is in all practical solar cells), then the left hand side of this inequality will be close to 1, as the integral is dominated by the value close to the bandgap (due to the exponential decay). For small δ the right hand side of this equation will be much less than 1, as $\Phi_{AM1.5}(E)$ is non-zero well above the bandgap of most solar cells. Therefore, the above inequality is satisfied, showing that it is possible simultaneously to increase V_{oc} and reduce efficiency in a solar cell.

Supplementary Note 5 – governing equations of a light emitting diode (LED)

We use the same governing equations as outlined in supplementary note 3 but set $J_{sc} = 0$ and reverse the sign of $J(V)$ as it is now an injection current. That is

$$J(V) = k_1 \left(e^{\frac{qV}{2k_BT}} - 1 \right) + J_0 \left(e^{\frac{qV}{k_BT}} - 1 \right) + k_3 \left(e^{\frac{3qV}{2k_BT}} - 1 \right).$$

Here we can split the light out from the LED, $J_0 \left(e^{\frac{qV}{k_BT}} - 1 \right)$, into that which leaves from the front and back of the LED. We define that which leaves the front of the LED as $J_{0,f} \left(e^{\frac{qV}{k_BT}} - 1 \right)$ where $J_{0,f} = q\pi \int \Phi_{bb}(E) a_{front}(E) dE$ (and $a_{front}(E)$ is defined in Supplementary Table 1).

We fabricated CsPbBr$_3$ thin films and measured absorption coefficient and refractive index using ellipsometry, with the same data analysis as the approach by Shin et al. [5]. We fitted an Urbach tail to photoluminescence data for the absorption coefficient in the below bandgap region (data and fit presented in Figure S19). We assume that Auger recombination rates are the same as in the MAPbI$_3$ system, as these have been observed to be similar across a range of different perovskites [6–8]. Lastly, our simulations require some value for the doping density. We assume an intrinsic semiconductor and note that background doping density, $n_i = A e^{-\frac{E_g}{2k_BT}}$, where A is a constant based on the shape of the valence and conduction bands near the band edge. As all 3D perovskites have approximately the same bandstructure near the bandgap we use MAPbI$_3$ data to estimate the background doping density in CsPbBr$_3$ as 0.042cm^{-3}, a much lower value due to the larger bandgap in CsPbI$_3$. We again assume no Stokes shift so the previously used absorptance models can now be applied as emittance models. The final point to note is that as charges are injected in an LED, previous expressions for the PLQE are replaced by expressions for the electroluminescence quantum efficiency ($ELQE_{ext}$) which is equal to (assuming balanced injection of electrons and holes),

$$ELQE_{ext}(V) = \frac{J_0 \left(e^{\frac{qV}{k_BT}} - 1 \right)}{J(V)}.$$

To calculate the luminous emittance we calculate $\pi \int E\Phi_{bb}(E)\Theta(E) a_{front}(E) dE$, where $\Theta(E)$ is the photopic luminosity function. For the case of emission into a small 2.5° angle we assume approximately isotropic emission so divide by the solid angle of emission, 5.98×10^{-3}.

Supplementary Table 1

Name	
Direct	$$a_{direct}(E) = \frac{T_1(1 - e^{-\alpha t})(1 + (1 - T_2)e^{-\alpha t})}{1 - (1 - T_1)(1 - T_2)e^{-2\alpha t}}$$ $$a_{front}(E) = 2n^2 \int_0^{\tilde{\theta}} \frac{T_1\left(1 - e^{-\frac{\alpha t}{\cos(\theta)}}\right)\left(1 + (1 - T_2)e^{-\frac{\alpha t}{\cos(\theta)}}\right)}{1 - (1 - T_1)(1 - T_2)e^{-\frac{2\alpha t}{\cos(\theta)}}} \cos(\theta)\sin(\theta)\, d\theta$$ Here T_1 and T_2 are the front and rear transmission coefficients. $\sin(\tilde{\theta}) = \frac{\sin(\theta_{out})}{n}$, where in our simulations $\theta_{out} = 90°$, except when considering light emission into only a small angle, in which case it is set to 2.5° in all simulations in the main text. To calculate $a_{back}(E)$, T_1 and T_2 are exchanged in the above expression. $a(E) = a_{front}(E) + a_{back}(E)$.
Randomised	$$a_{direct}(E) = \frac{4\alpha n^2 t T_1}{T_1 \sin^2(\tilde{\theta}_{out}) + T_2 + 4\alpha n^2 t}$$ $$a_{front}(E) = \frac{4\alpha n^2 t T_1}{T_1 + \frac{T_2 + 4\alpha n^2 t}{\sin^2(\theta_{out})}}$$ $$a_{back}(E) = \frac{4\alpha n^2 t T_2}{T_1 + \frac{T_2 + 4\alpha n^2 t}{\sin^2(\theta_{out})}}$$ All terms defined are the same as in the Direct model. From statistical ray optics, representing a rough surface. In Yablonovitch's derivation all light in the semiconductor is assumed indistinguishable, so $a_{direct} = a$ when there is interaction over a full 2π hemisphere [9].
Maximal	$$a_{direct}(E) = \frac{4\alpha n^2 t}{\sin^2(\theta_{out})} \; if < 1, else\; 1$$ $$a(E) = 4\alpha n^2 t \; if < \sin^2(\theta_{out}), else\; \sin^2(\theta_{out})$$ Corresponds to a maximum in $\eta_{esc}(E)$, representing a surface which absorbs the maximum possible incident light at all energies (c.f. equation 1). Assumed $a_{direct} = a$ in the same way as 'Randomised' as these agree when $\alpha \to 0$. We do not consider transmission coefficients in this model.

Supplementary table 1. The absorptance options used in modelling solar cell efficiency.

Supplementary References

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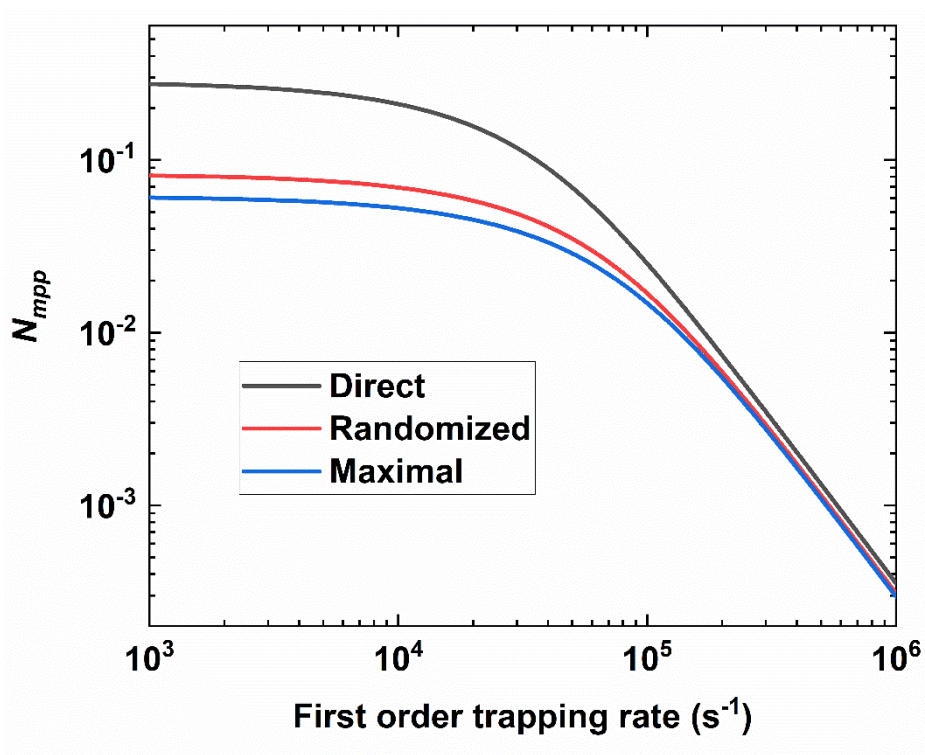
[9]   E. Yablonovitch, J. Opt. Soc. Am. **72**, 899 (1982).
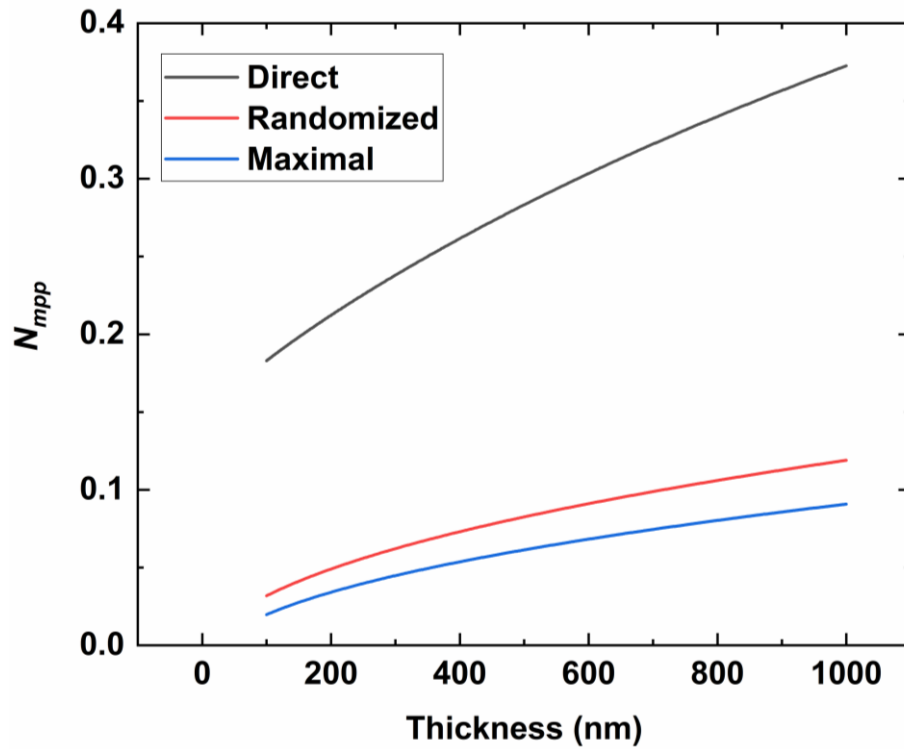
Figure S1. The number of photon recycling events at maximum power point with film thickness for the three absorptance models considered, with no charge trapping.
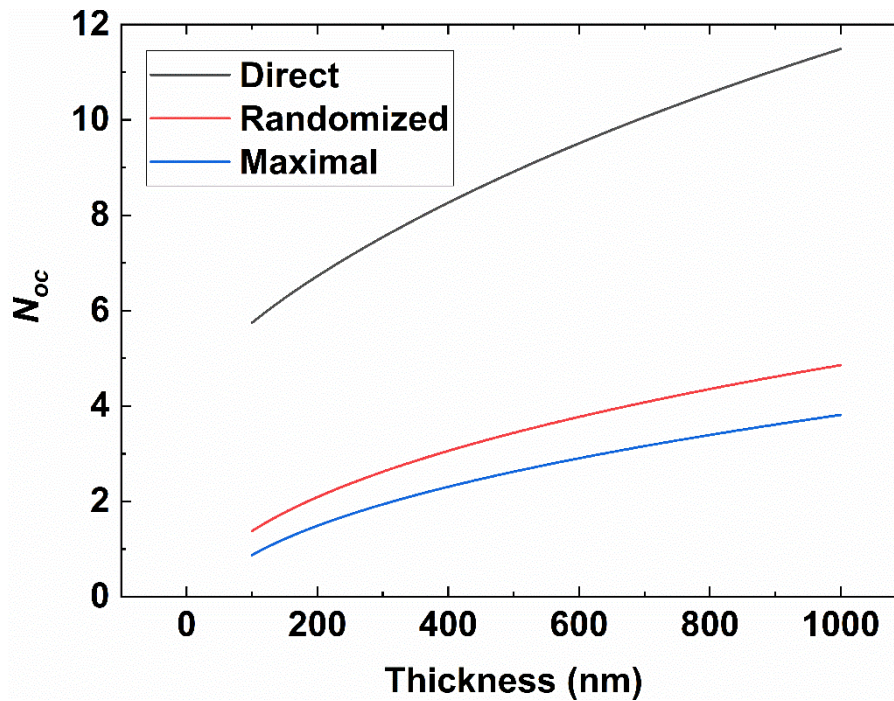
Figure S2. The number of photon recycling events at open circuit voltage versus thickness, with no first order loss rate for the three absorptance models considered.
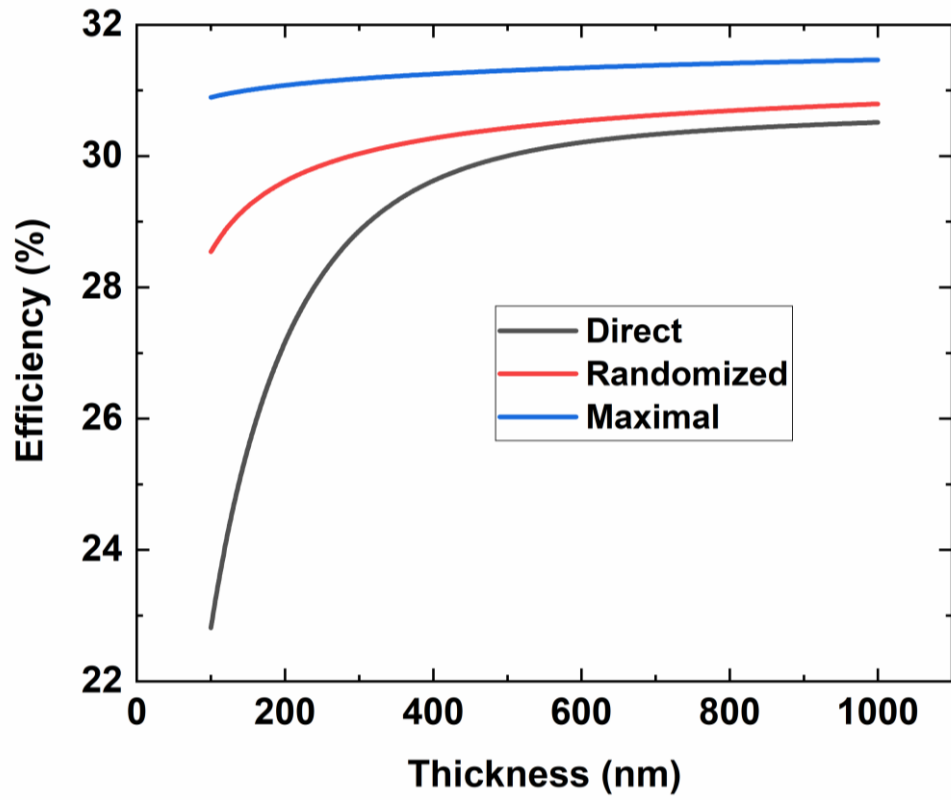
Figure S3. Efficiency with thickness in the case of no charge trapping.
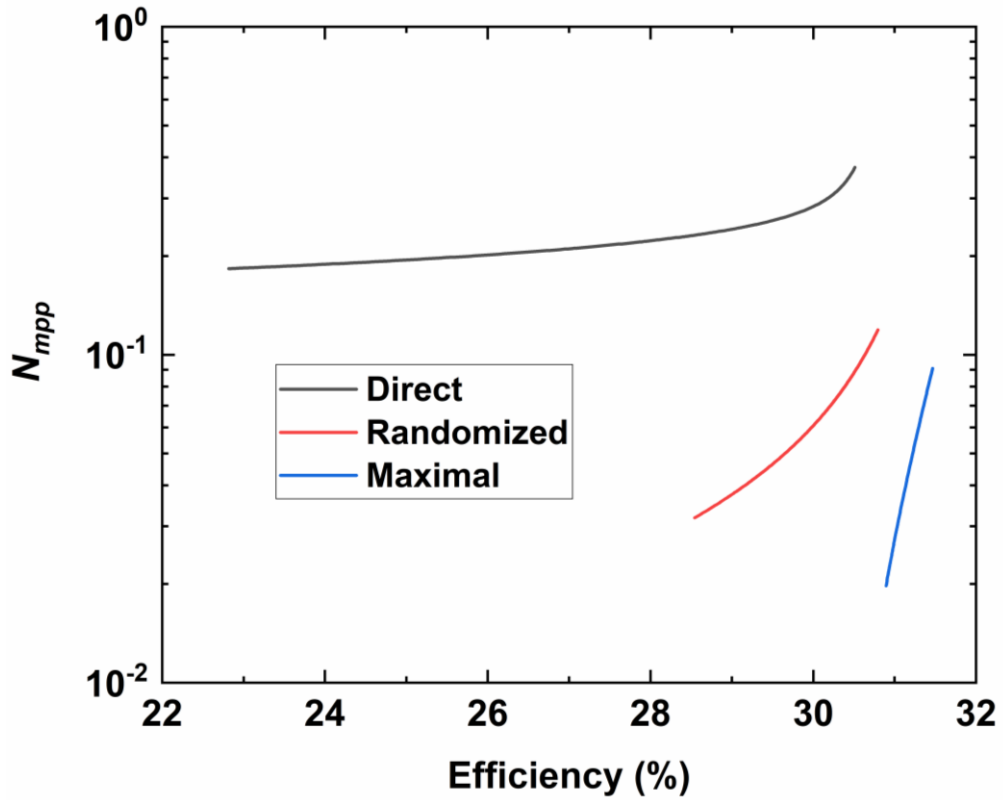
Figure S4. Number of photon recycling events at maximum power point versus efficiency when varying the solar cell thickness (with no first order trapping).
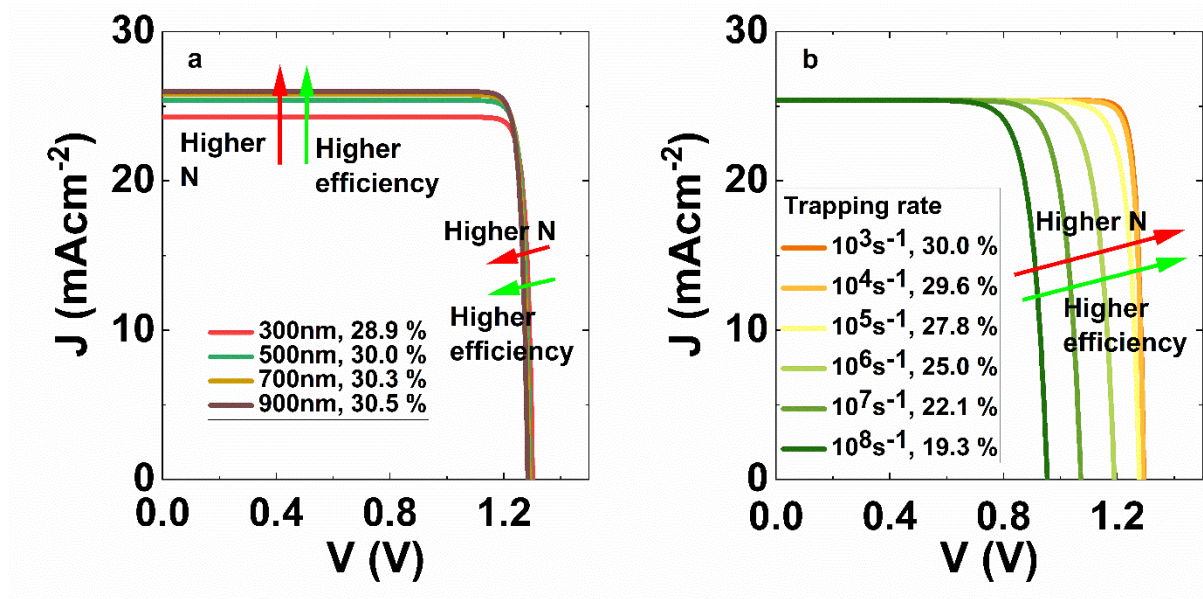
Figure S5. Current voltage curves for a) different thicknesses, with no charge trapping and b) different charge trapping rates for a 500 nm thick film. In all cases a 2π interaction hemisphere with the surroundings is modelled. Efficiencies are marked on legends, and higher efficiency and and number of photon recycling events (N) are marked on plots with green and red arrows respectively.
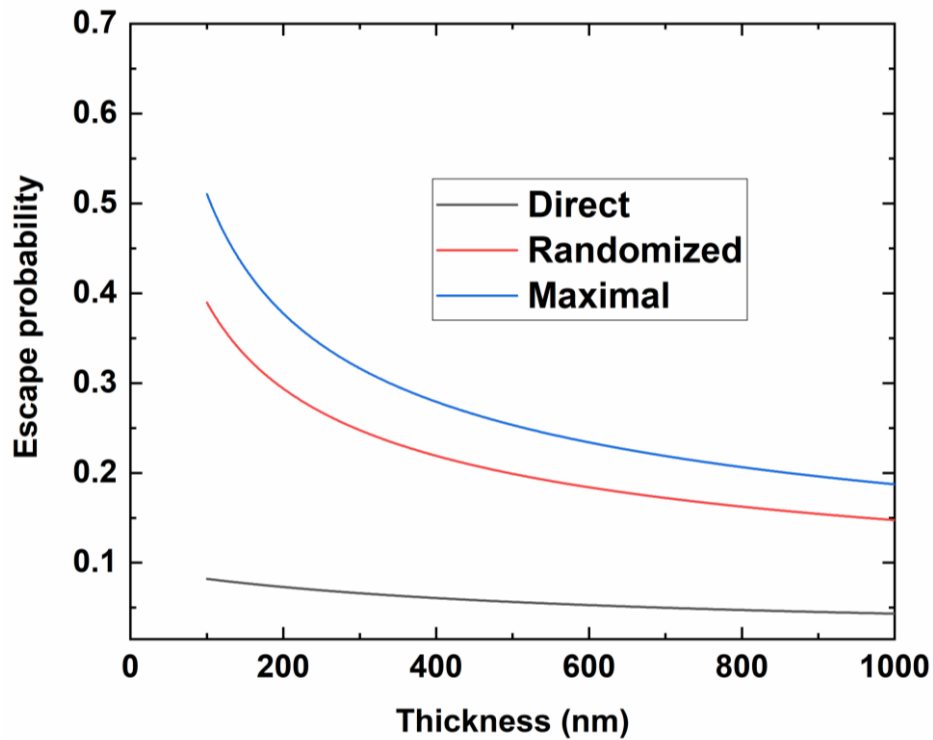
Figure S6. Escape probability with thickness.
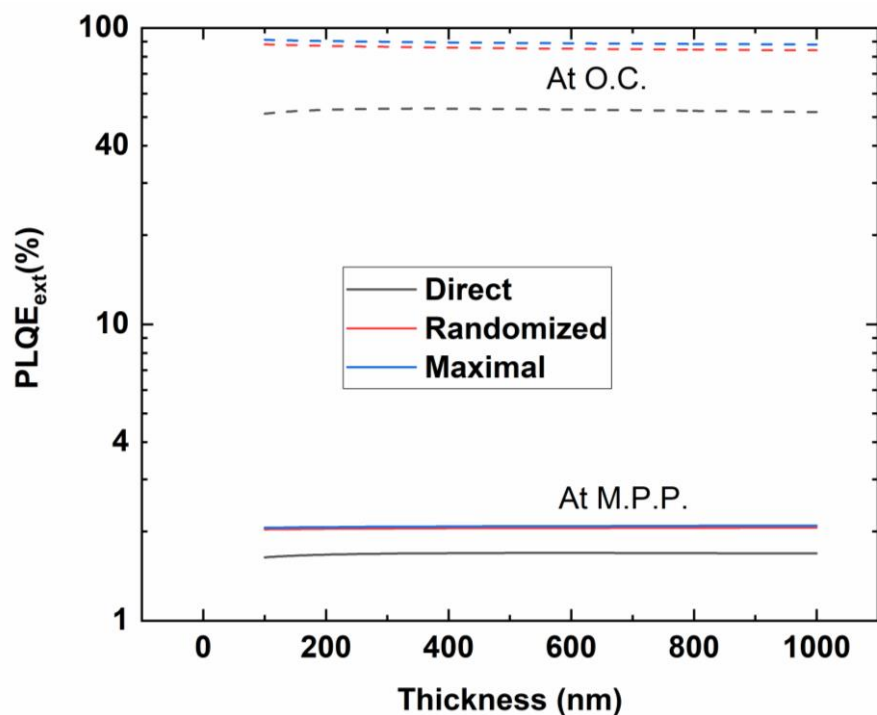
Figure S7. External PLQE with thickness at open circuit (O.C.) and maximum power point (M.P.P.). In all plots there is no first order trapping rate. The PLQE is less than 100 % in all cases due to Auger recombination and in the case of maximum power point also because of charge extraction.

Figure S8. The number of photon recycling events at maximum power point with charge trapping rate the three absorptance models considered, for a 500 nm film.
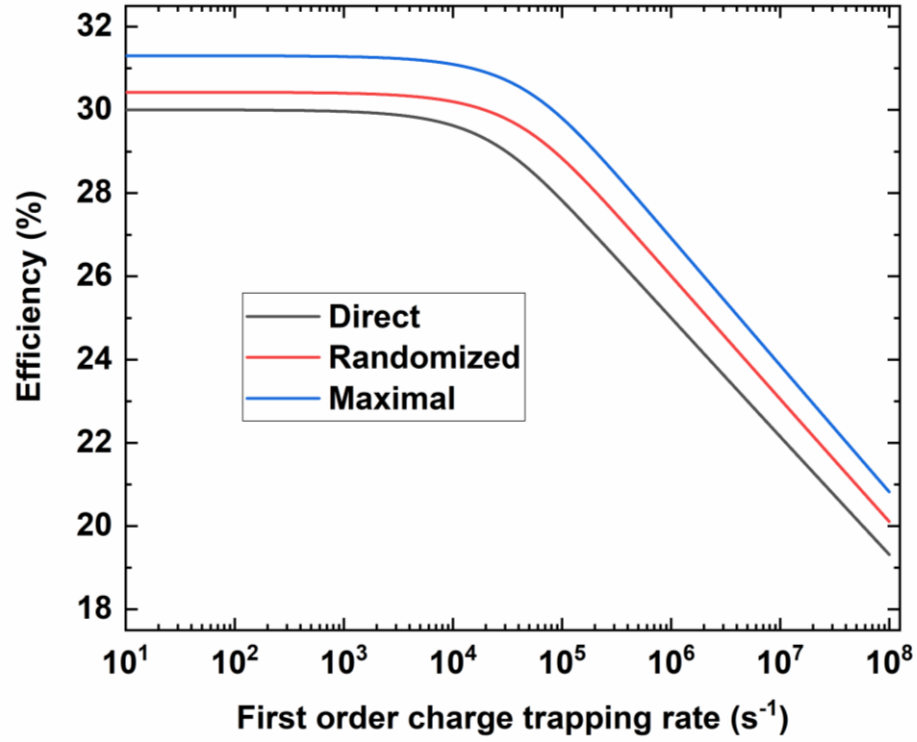
Figure S9. Efficiency with charge trapping rate for a 500 nm film, for all three absorption models.
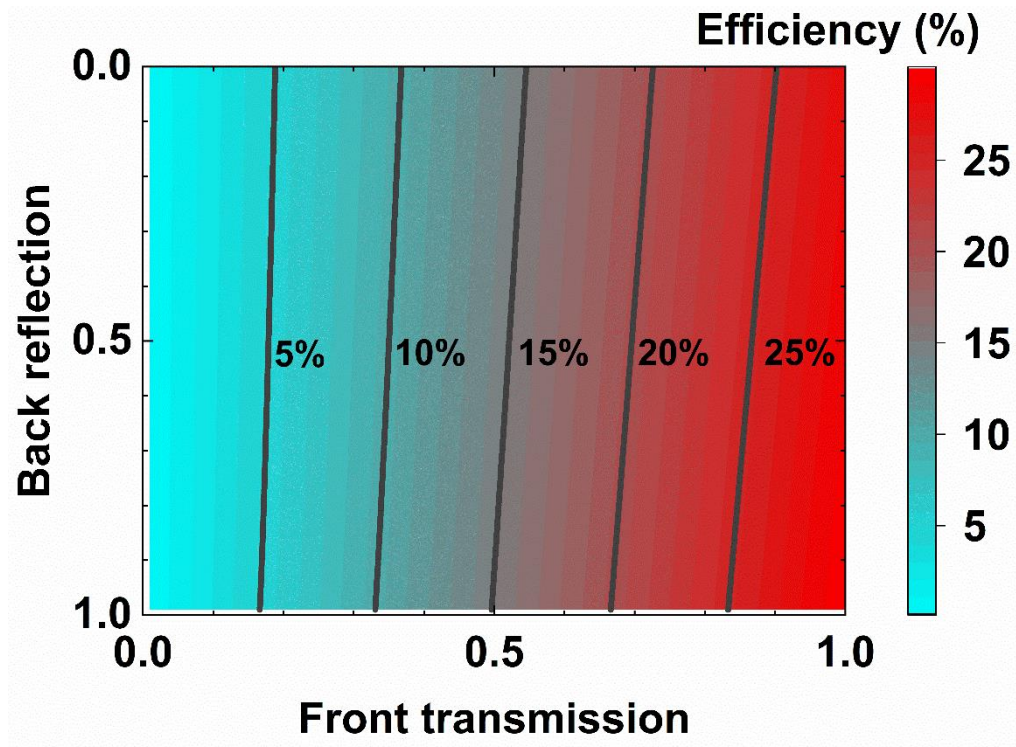
Figure S10. Efficiency with front transmission and back reflection coefficients for the Direct absorptance model. Specific efficiencies are marked on the plot as grey lines.

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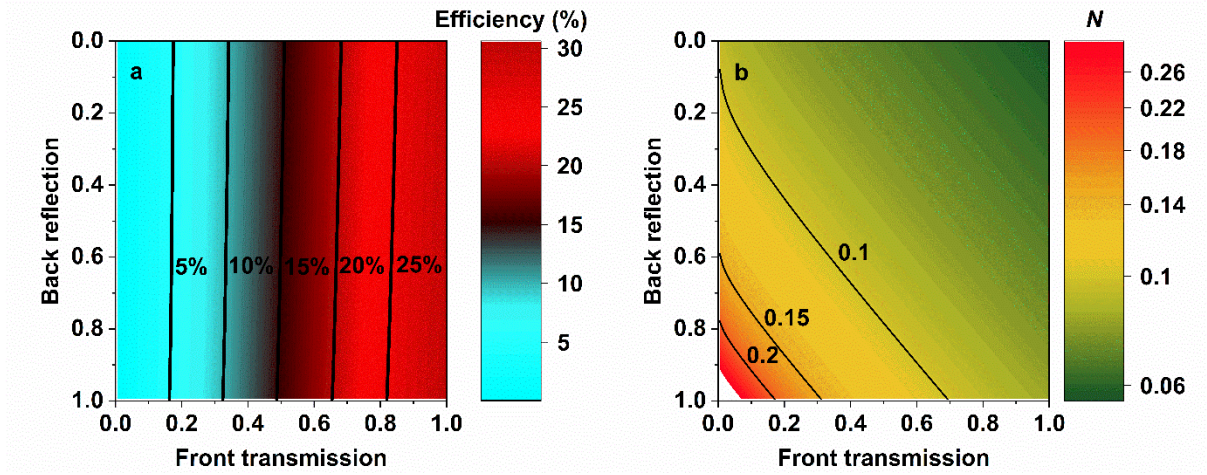
Figure S11. The efficiency and number of photon recycling events are presented in a) and b) for Randomized absorption model with non-ideal front transmission and back reflection.
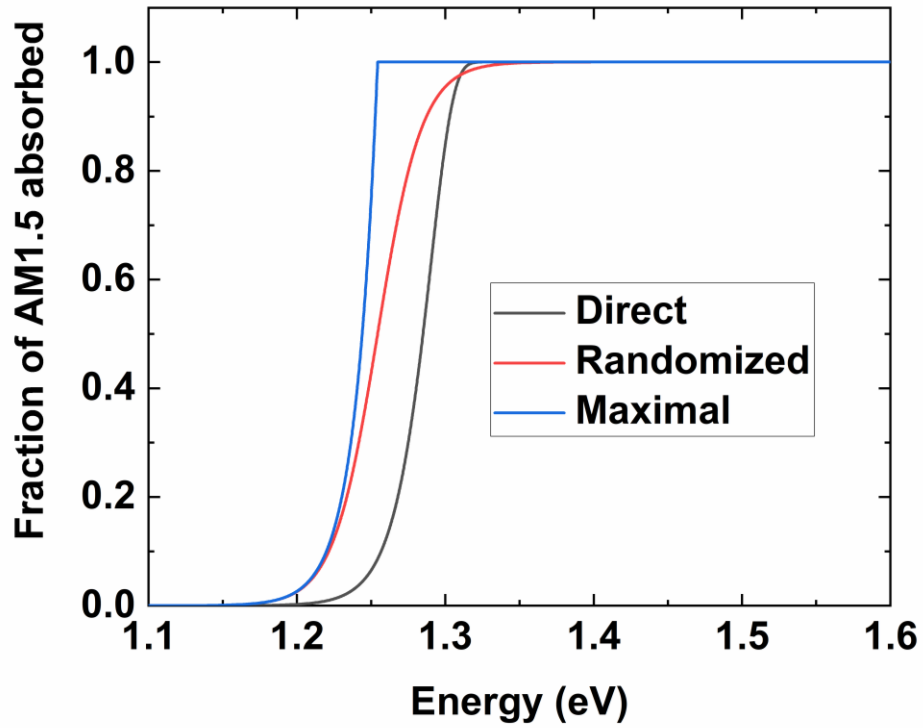
Figure S12. Direct absorptance plotted as a function of energy for the three different absorptance options considered in the main text, for a 500 nm film.
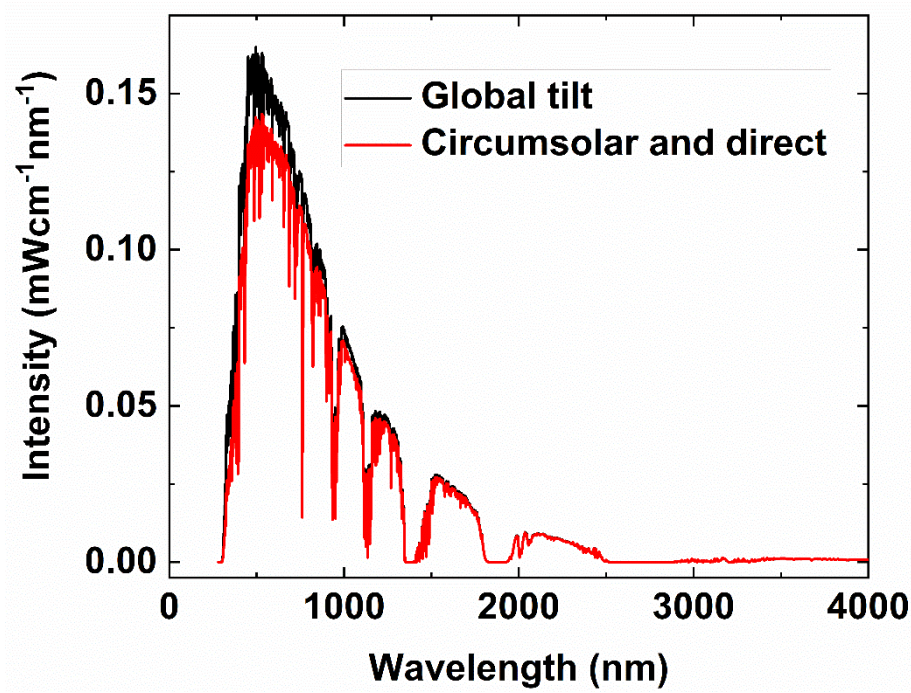
Figure S13. 'Global' and 'circumsolar and direct' AM1.5 spectra. Global spectra are used in all simulations where a solar cell interacts with a full 2π hemisphere, while circumsolar and direct are used for solar cells which only interact with 2.5° about the normal to their surface, corresponding to the solid angle of circumsolar radiation.
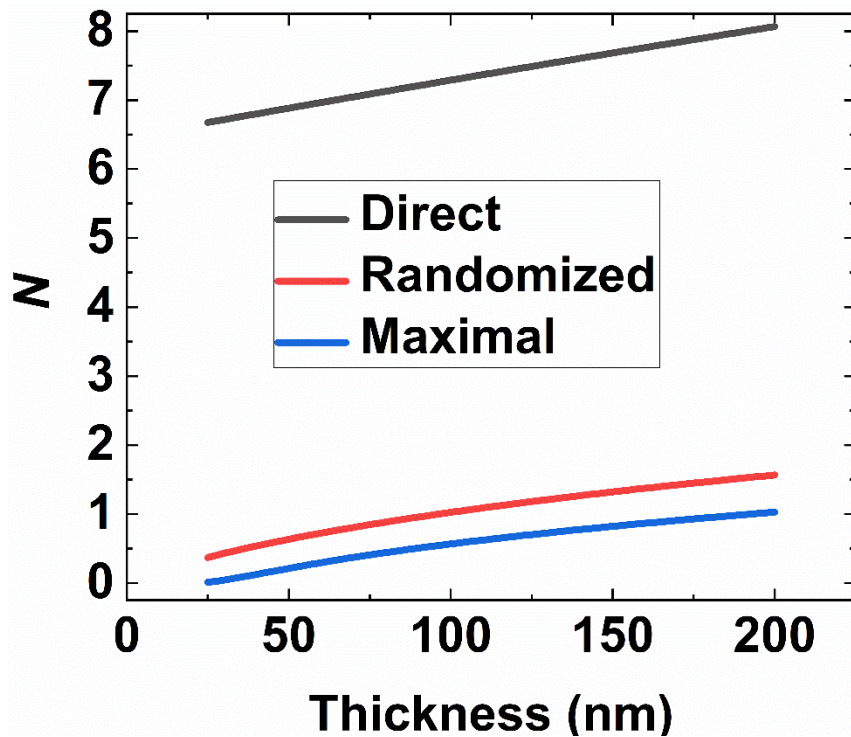
Figure S14. Number of photon recycling events with thickness in an LED for three emittance models. The voltage is set in all simulations to be 1.998 V, which gives 1000 lm m^{-2} at 100 nm thickness in the Direct model.
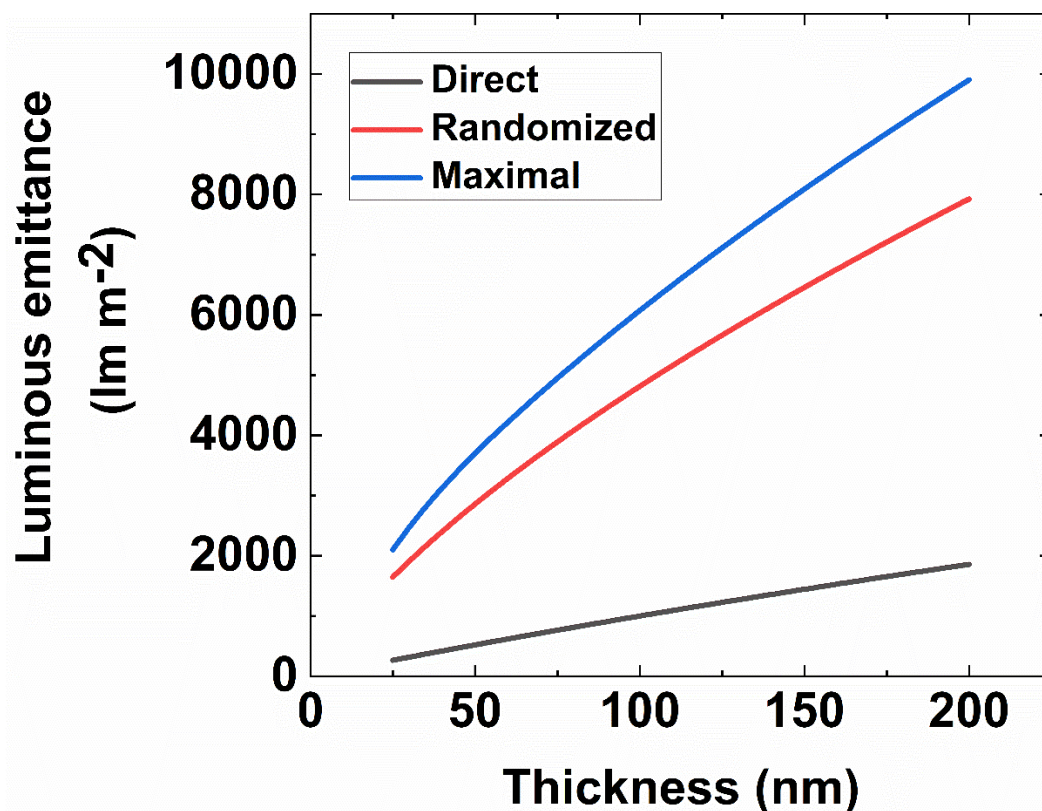
Figure S15. Luminous emittance with thickness for all emittance models considered.
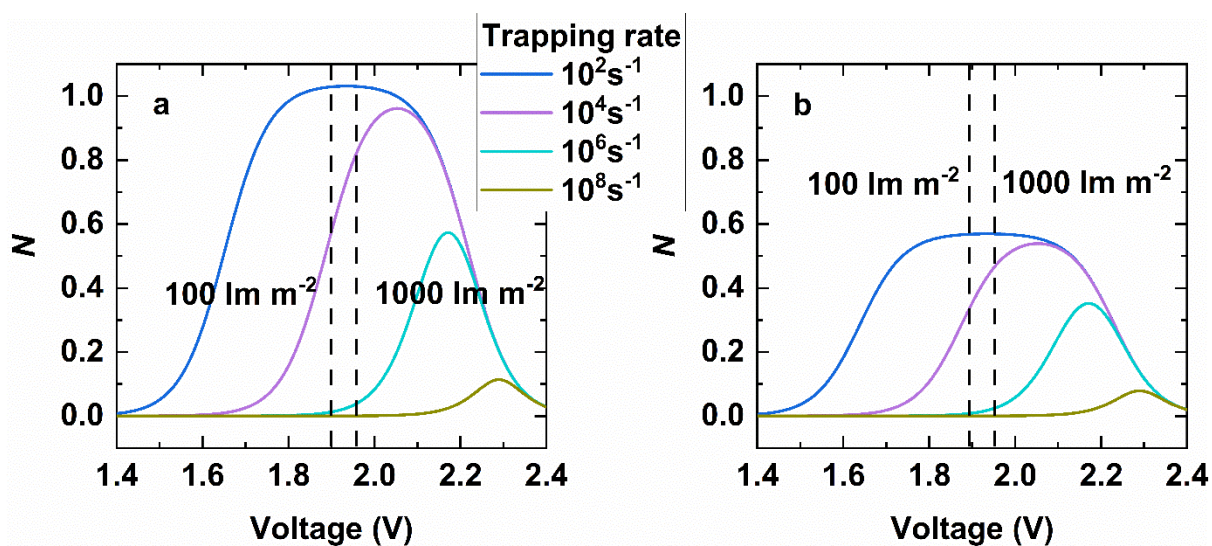

Figure S16. Number of photon recycling events as a function of applied voltage for different charge trapping rates are presented in a) and b) for Randomized and Maximal emittance models respectively. Relevant luminous emittances are marked at corresponding voltages.
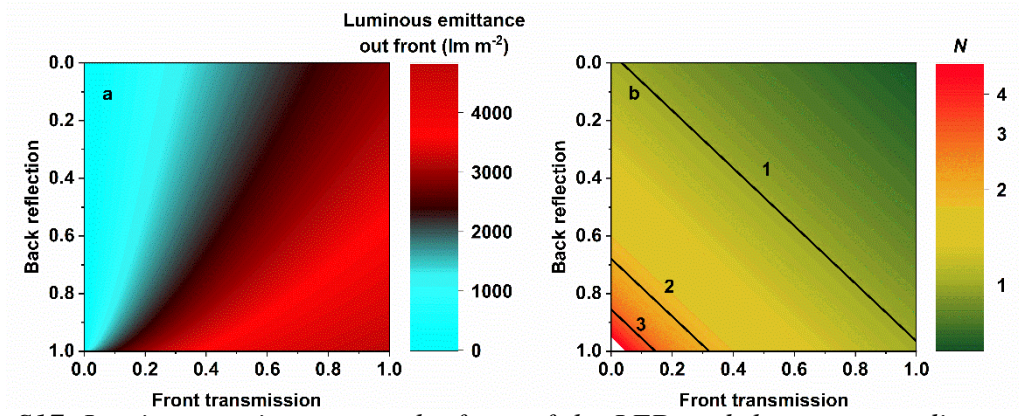
Figure S17. Luminous emittance out the front of the LED and the corresponding number of photon recycling events as a function of front transmission and back reflection coefficients for Randomized emittance model are presented in a) and b) respectively.
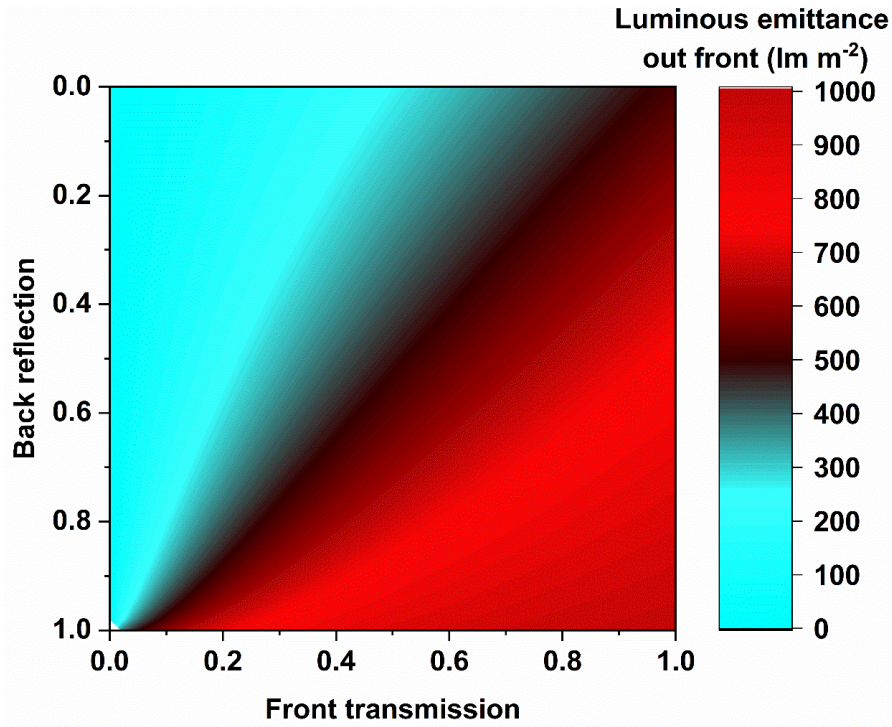

Figure S18. Luminous emittance out the front of the LED as a function of front transmission and back reflection coefficients for the Direct emittance model.
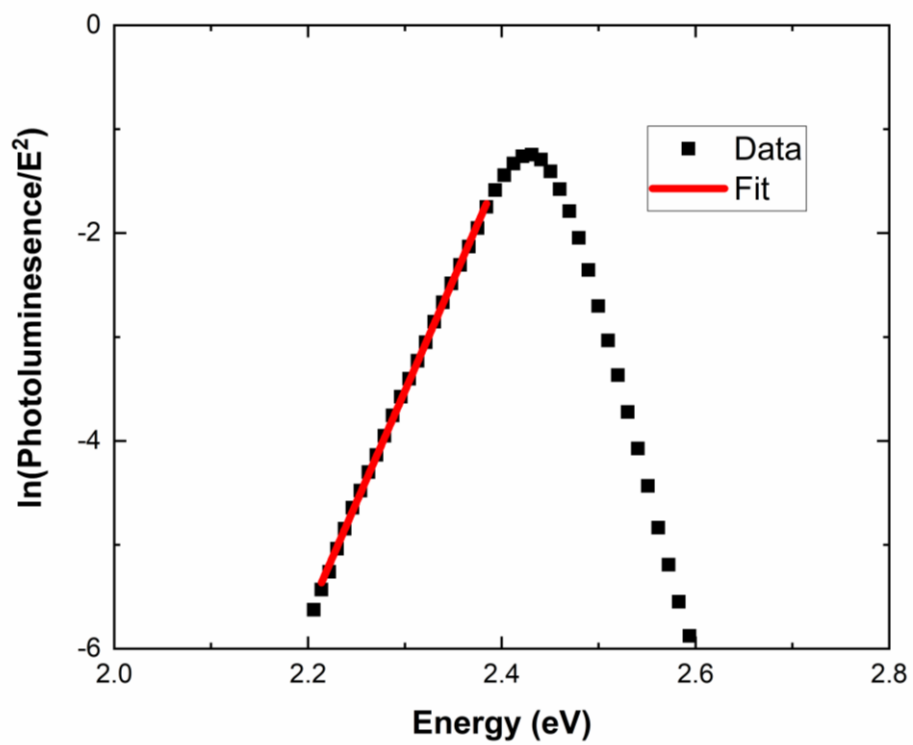
Figure S19. We present an Urbach fit to the tail of photoluminescence data, for a CsPbBr₃ sample.