Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplemental Information

for

The role of dark exciton reservoir in the luminescence efficiency of two-dimensional tin iodide perovskites

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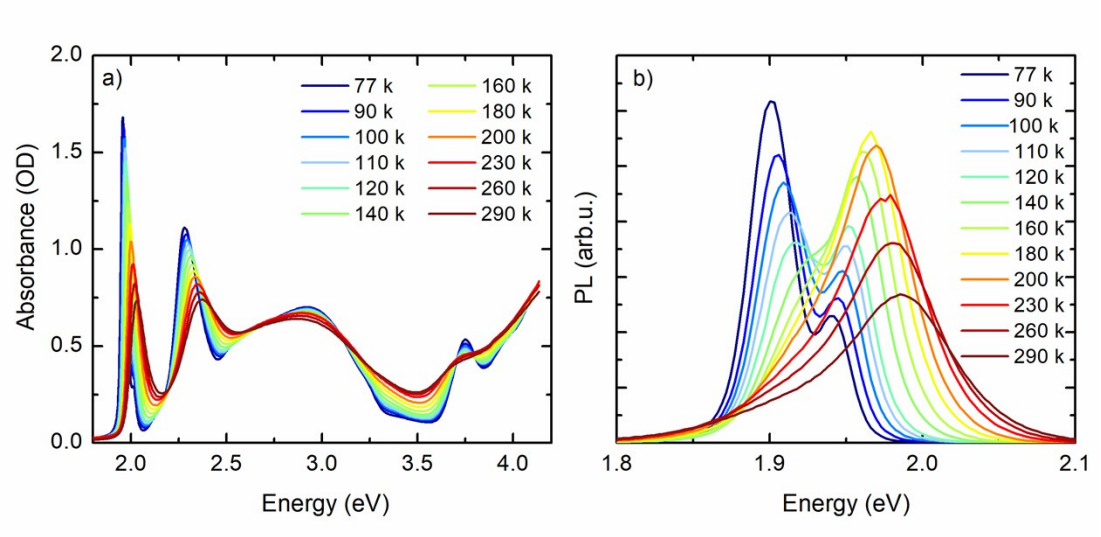

Figure S1 Temperature dependent a) absorbance and b) photoluminescence of PEA_2SSnI_4 between 77 K and 300 K.

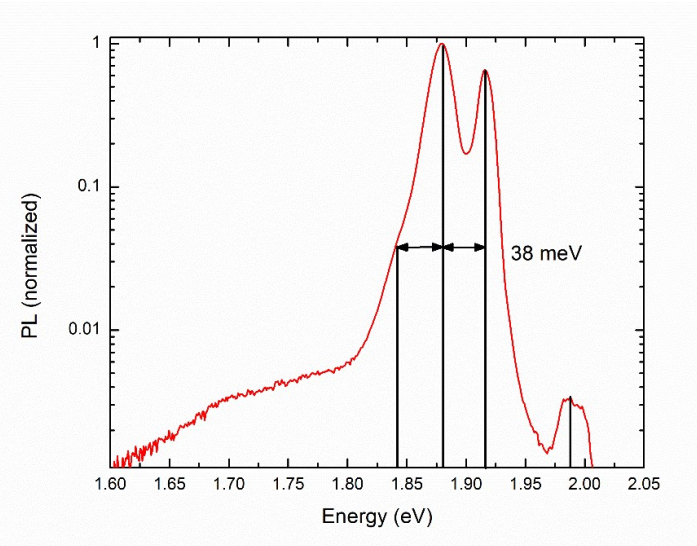

Figure S2 PL spectrum at 18 K, shown in logarithmic scale: the sample emission shows at least excitonic peaks together with a broad shoulder on the red side. The main excitonic peaks are separated by 38 meV, while the peak appearing at 1.98 eV appears to be further apart due to strong self-absorption at 1.97 eV.

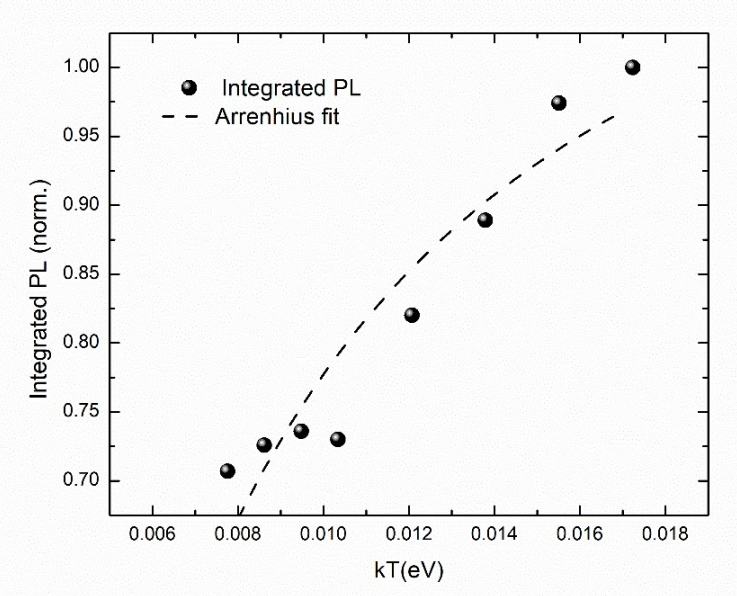

Figure S3 Arrenhius fit of the photoluminescence intensity integrated between 485 -650 nm in a temperature range between 77 K and 200 K, where the total Pl intensity reaches a maximum: the activation energy obtained from the fit is 10 meV +/- 4 meV.

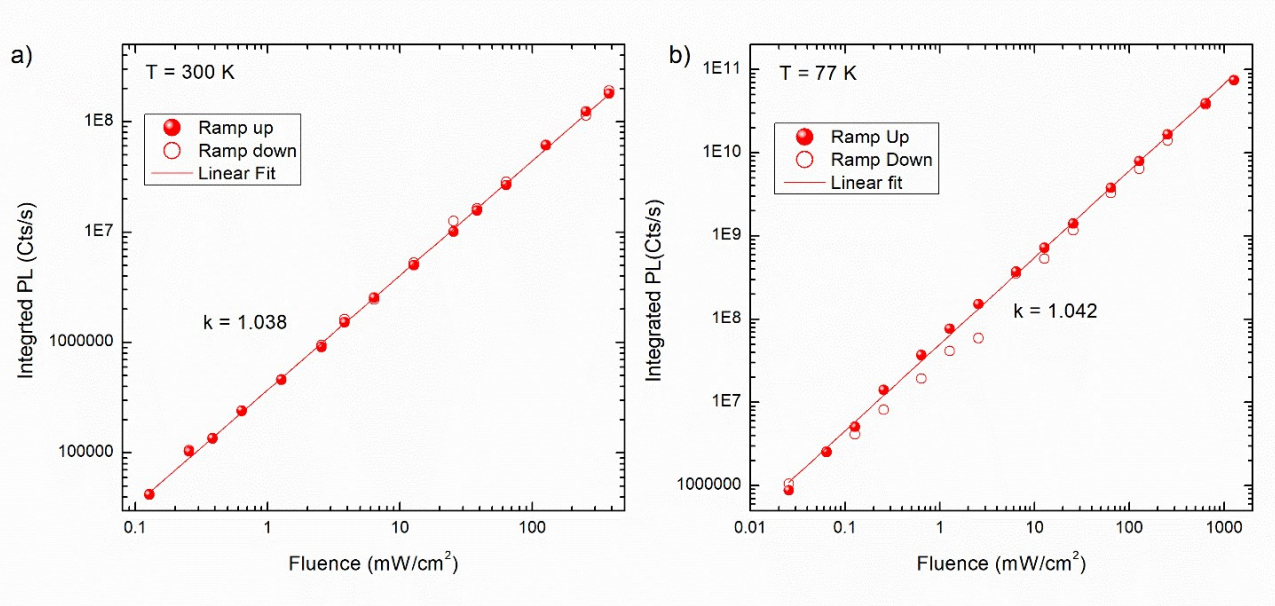

Figure S4 Fluence dependence of the photoluminescence intensity (integrated between 485 nm and 650 nm) at a) room temperature and b) 77 K. The data has been fitted with a linear function $I_{PL} = m\ I_{pump}^{k}$.

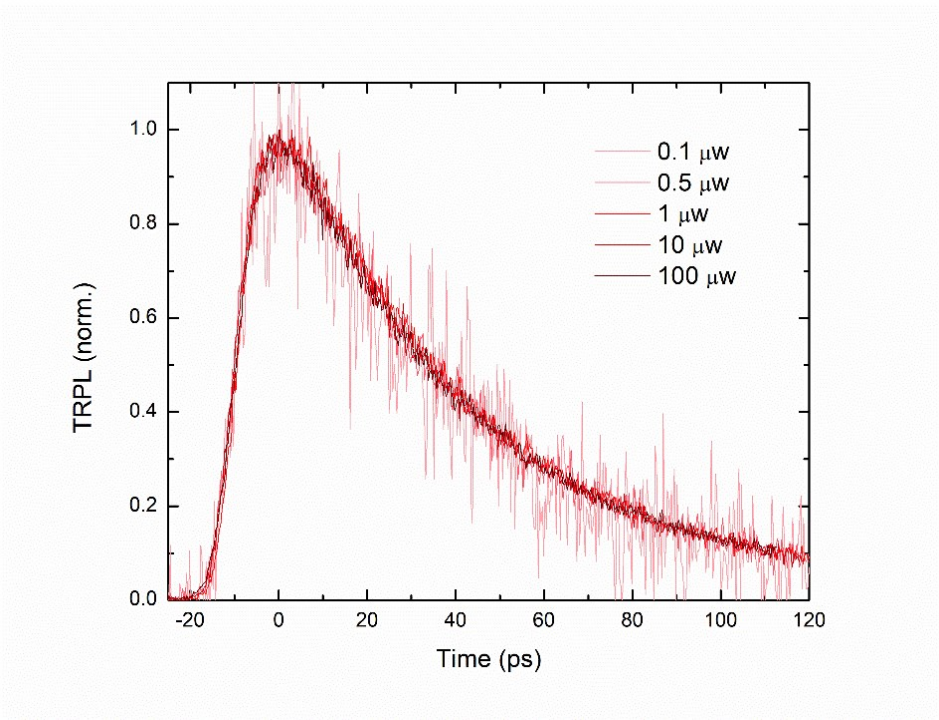

Figure S5 Fluence dependence of tr-PL decays at temperature 5 K, showing no change in exciton dynamics over three orders of magnitude of pump fluence.

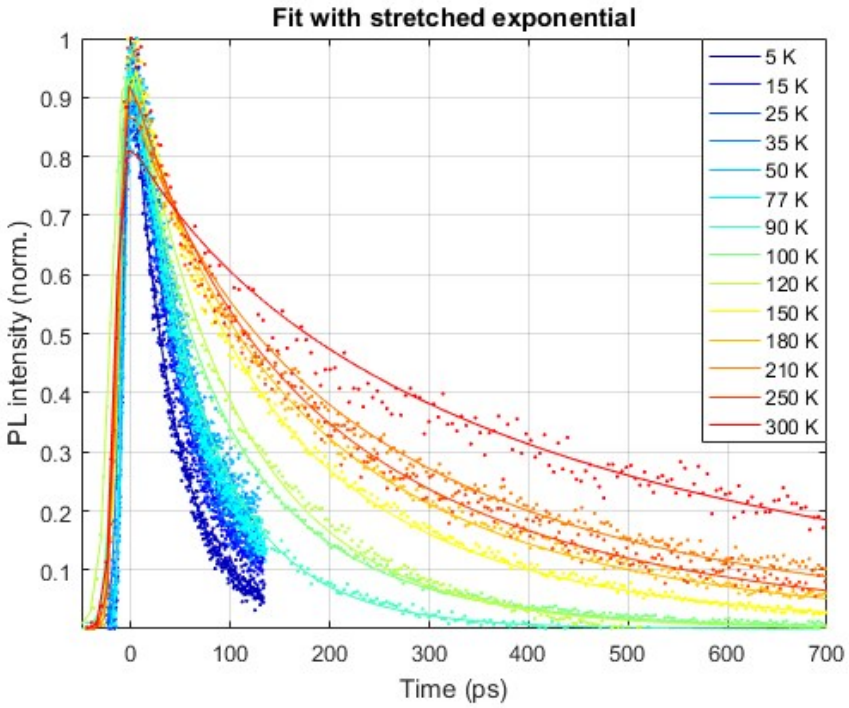

Figure S6 Fit of the PL decay at different temperature using a stretched exponential function.

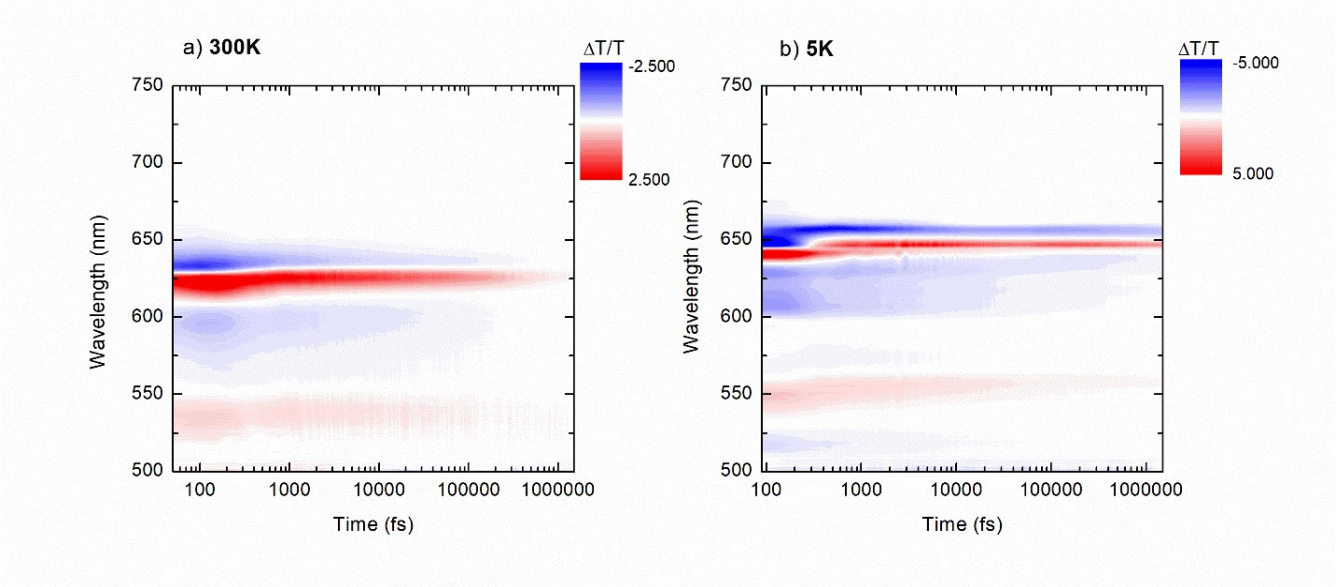

Figure S7 Transient absorption maps taken at a) room temperature and b) 5 K: for both temperatures the temporal axis extends from - 10 fs to 1.5 ns.

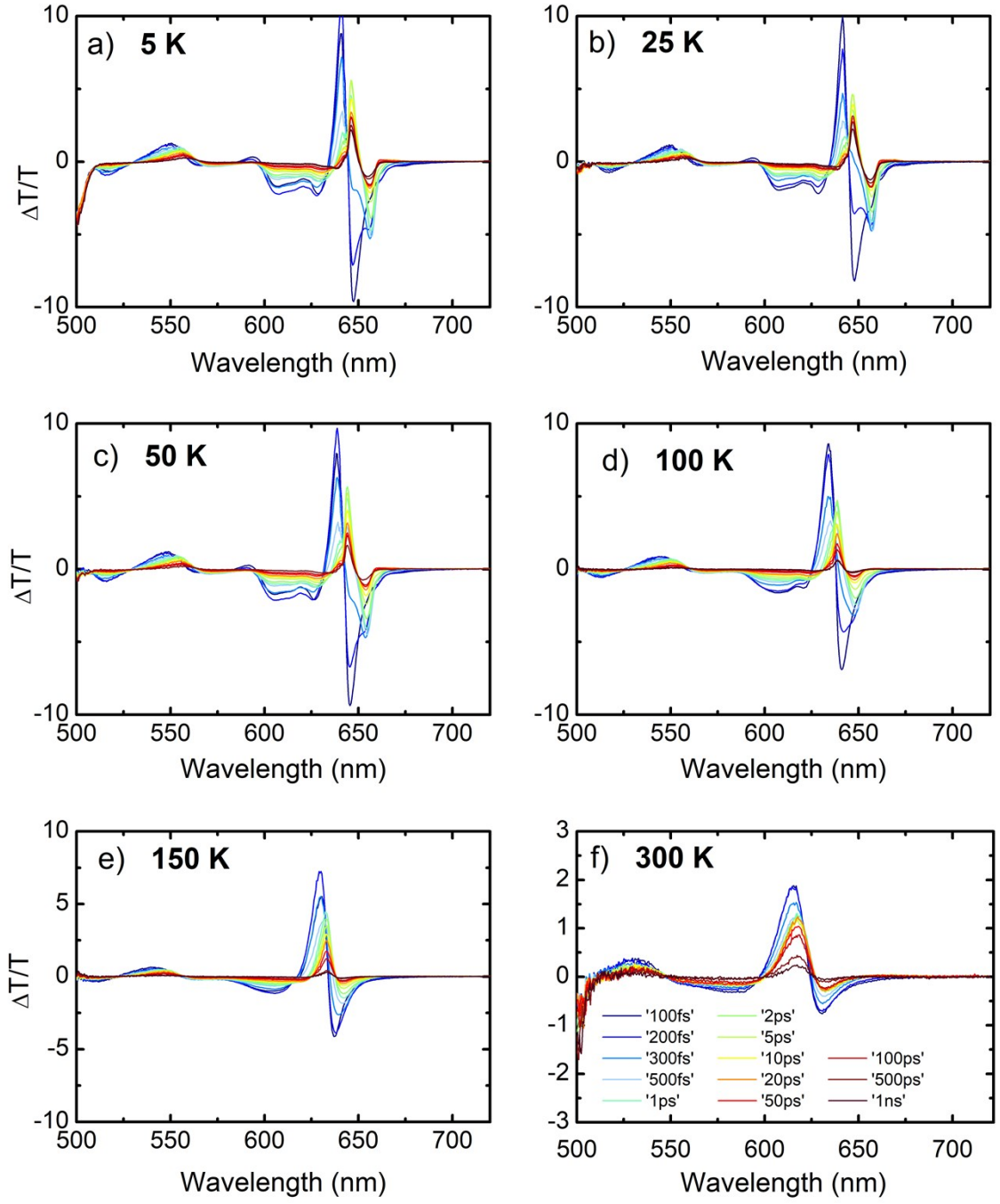

Figure S8 Transient absorption spectra at selected delays at temperatures a) 5 K, b) 25 K, c) 50 K, d) 100 K, e) 150 K, f) 300 K.

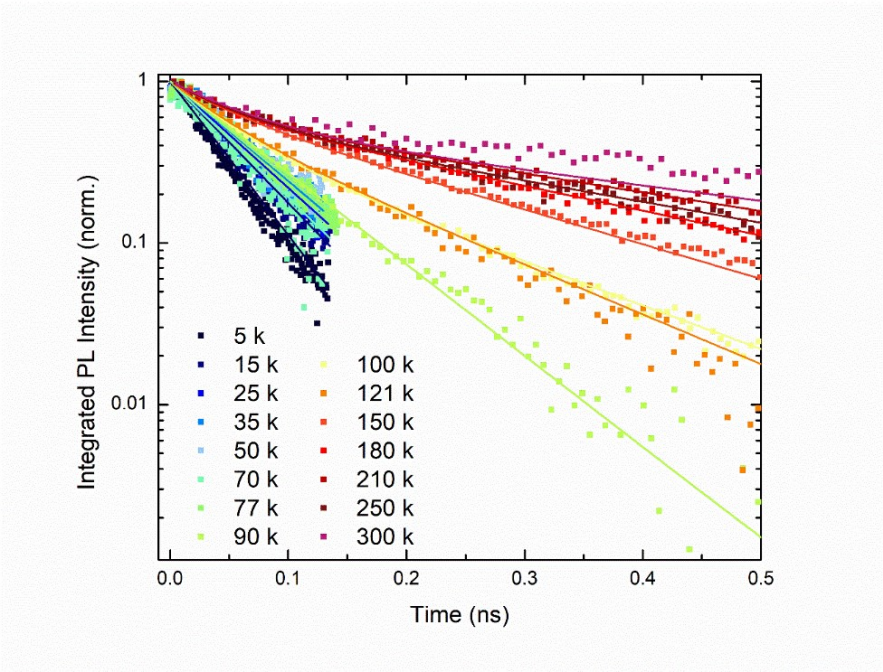

Figure S9 Fitting of PL decays from 5 K to 300 K based on the rate equation model including radiative exciton recombination and transfer to a dark state and back.

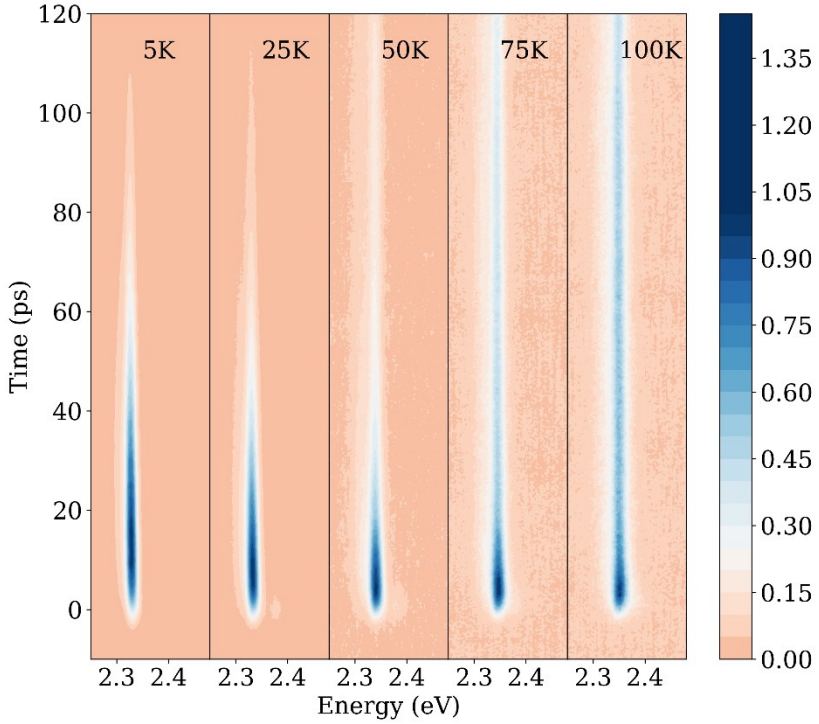

Figure S10 Time-resolved PL of a PEA_2PbI_4 thin film: similar to its Sn counterpart, an increase of excitonic emission lifetime with temperature is observed between 5 K and 100 K.

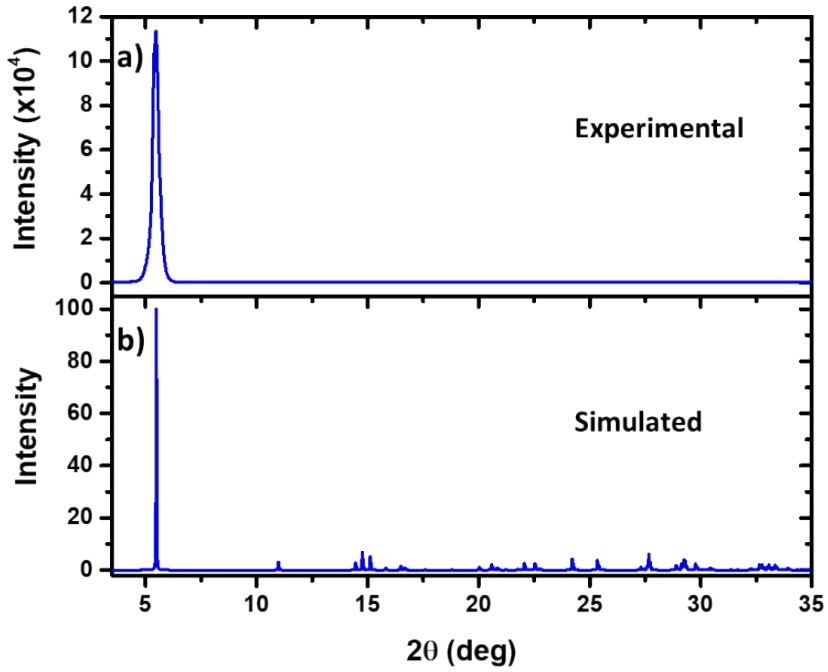

Figure S11 a) Experimental XRD pattern measured on a PEA_2SnI_4 film spin-coated from a 0.2M solution in DMF. b) Simulated XRD pattern of PEA2SnI4 using the crystal structure reported by Y. Takahashi et al (Chem. Mater. 2007, 19, 25, 6312-6316).

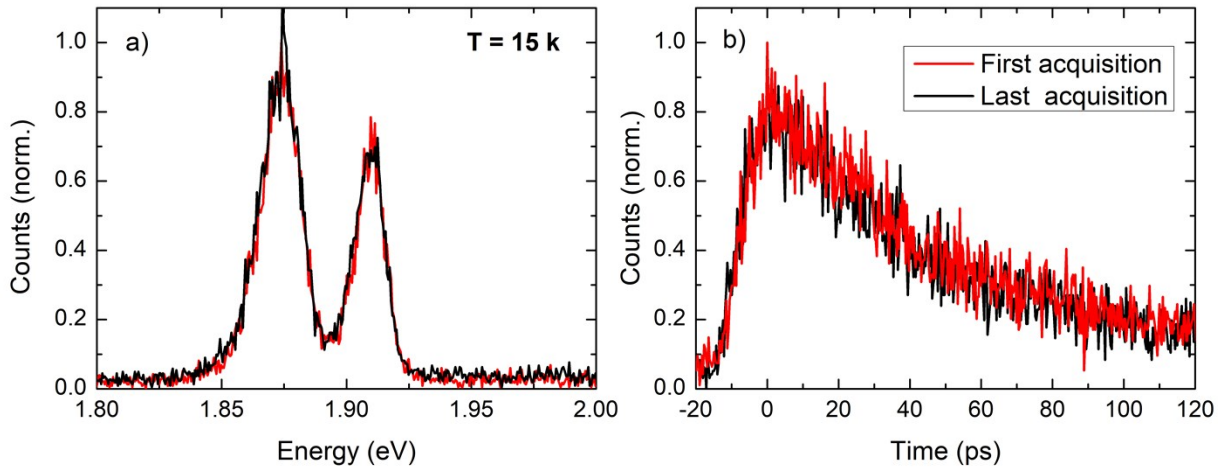

Figure S12 Photostability of TRPL measurements: the red and black lines show data acquired respectively during the first and last 5 minutes of integration (typical integration time: 40 minutes), comparing the resulting a) spectra and b) emission decay recorded. This data set in particular shows a measurement at T = 15 K in 120 ps measurement window, with 2 ps time resolution: at the highest resolution available in our set-up, both spectra and emission dynamics appear unchanged over the course of a measurement, confirming that photodegradation does not play an important role in this experimental regime.

Stretched exponential decay fitting

The TRPL decays were fit using a stretched exponential function multiplied by a growth term: $I(t) = \frac{I_0 e^{-(t/\tau)^{\beta}}}{1 + g\, e^{(t - t_0)}}$ where *g* is the growth rate and t_0 is the maximum intensity. Time zero in the measurement is defined for all measurements as the peak intensity for the X2 feature, which occurs earlier then the peak of X1 when the two are spectrally resolved. A stretched exponential is chosen to describe the decays to reflect the assumption that the excited population is not described by a single well-defined, but rather by a decay rate distribution, accounting for spatial variability in the sample as well as evolution in time of the decay rate and presence of multiple decay processes. The decay time τ represents the average value of the distribution resulting in the observed decay, while the stretch factor β is related to its width. A stretch factor value close to 1 corresponds to a quasi-monoexponential decay, i.e. a narrow single valued decay distribution, while a value of β significantly lower than 1 corresponds to a broad distribution of decay rates. Results of the fits are reported in table S1.

Table S1: stretched exponential fit results

Temperature	I_0	τ (ps)	t_0 (ps)	*g*	β
5 K	1.61 ± 0.09	41.21 ± 2.65	12.09 ± 0.18	2.64 ± 0.10	0.97 ± 0.05
15 K	1.68 ± 0.12	48.62 ± 3.99	15.31 ± 0.22	3.06 ± 0.12	0.92 ± 0.05
25 K	1.42 ± 0.08	63.60 ± 4.07	15.17 ± 0.22	2.78 ± 0.14	1.02 ± 0.06
35 K	1.40 ± 0.10	67.75 ± 5.03	13.32 ± 0.33	3.53 ± 0.19	1.03 ± 0.08
50 K	1.29 ± 0.08	74.60 ± 5.17	13.07 ± 0.31	3.14 ± 0.19	1.06 ± 0.08
60 K	1.28 ± 0.03	66.48 ± 1.66	15.61 ± 0.27	2.55 ± 0.22	1.10
77 K	3.97 ± 0.08	37.03 ± 0.54	42.16 ± 0.19	4.78 ± 0.13	0.70
90 K	2.97 ± 0.47	48.94 ± 8.51	38.74 ± 0.44	4.51 ± 0.25	0.80 ± 0.07
100 K	2.40 ± 0.03	56.71 ± 0.62	34.30 ± 0.15	4.15 ± 0.11	0.70
120 K	1.71 ± 0.26	97.27 ± 6.54	32.57 ± 0.28	5.56 ± 0.19	0.90 ± 0.04
150 K	1.84 ± 0.02	97.50 ± 1.26	36.47 ± 0.20	3.77 ± 0.17	0.70
180 K	1.54 ± 0.02	130.56 ± 2.00	34.20 ± 0.26	3.60 ± 0.22	0.70
210 K	1.32 ± 0.02	180.52 ± 3.51	33.80 ± 0.34	3.10 ± 0.30	0.70
250 K	1.44 ± 0.02	148.53 ± 3.08	30.34 ± 0.36	3.41 ± 0.31	0.70
300 K	1.05 ± 0.03	337.91 ± 15.19	28.54 ± 0.98	3.85 ± 0.85	0.70

Fitting of TRPL decay with rate equation model

To retrieve an estimate of the transfer rates appearing in our rate equations model, we fit the integrated PL intensity as a function of time we using the expression $I_{sim}(t) = \frac{k_{rad}}{n_o} n_X(t)$, where $n_X(t)$ is the population of the bright excitonic state X as a function of time. We estimated a value for the transfer rates by minimizing the quadratic error between the calculated $I_{sim}(t)$ and the experimental data. We assumed that the transfer rate to the dark excitonic state $k_{X \to D}$ and the radiative decay rate k_{rad} would show only a moderate temperature dependence, while allowing k_{BT}, the back transfer rate from the lower lying dark state to the bright state, to change with temperature over several orders of magnitudes. To achieve the best global fit for all three parameters at all temperatures we followed an approach akin to coordinate descent: we performed iterative fits while gradually reducing the parameter space for k_{rad} and $k_{X \to D}$ in a globally optimal range for all temperatures, and adjusting k_{BT} at each iteration to best fit the individual decays in our temperature scan.