Supporting Information

for *Adv. Mater. Interfaces*, DOI: 10.1002/admi.202101326

Interpreting the Time-Resolved Photoluminescence of Quasi-2D Perovskites

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Supporting Information

Title Interpreting the Time-Resolved Photoluminescence of Quasi-2D Perovskites

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Exciton emission efficiency:

The exciton emission efficiency does not affect the decay of the excitonic PL as the decay only depends on the total recombination rate. We fit our data using a constant to adjust for camera sensitivity and losses in our setup. We, therefore, overestimate the influence of excitons on the total PL of our mixed PL samples. The actual fraction of excitonic PL in our samples is likely lower than we assume. To overcome this limit in our observation a more advanced setup is necessary where not only the decay but also the emission efficiency (i.e. outcoupling) of the differently sized grains are considered.

**Figure S1.** Schematic illustrating the funneling process of excitons and free carriers into differently sized quantum wells above and below a critical thickness and separated by thin quantum wells prohibiting energy or charge transport between the two pools of radiatively emitting excited states.

**Figure S2.** Exciton PLQY simulated based on Equation 4 and approximation both using the same parameters as Figure 2.
**Figure S3.** Free charge carrier PLQY simulated based on Equation 8 and approximation both using the same parameters as Figure 2.

**Figure S4.** Comparison of simulated normalized PL dynamics in a) excitons and b) free charge carriers. The rates used in this illustration are chosen to lead to similar PL dynamics and are \( k_x = 1.25 \times 10^7 \text{ s}^{-1} \); \( \gamma_{E EA} = 2.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \); \( k_1 = 0.5 \times 10^7 \text{ s}^{-1} \); \( k_2 = 0.25 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \).

**Figure S5.** Initial densities derived from the maximum PL of the NMA\(_{0.8}\) and NMA\(_{1.0}\) perovskites presuming mainly bimolecular radiative emission with a) parabolic and b) cubic fit to account for losses during the excited-state funneling process.
Comments to Figure S5:

$N_0$ calculated from the excitation fluence and absorption does not take into account potential losses. EEA during the funneling process can lead to a decreased initial excited-state density in the emitting QWs. By presuming that the PL consists mainly of radiative bimolecular recombination we can estimate the initial density ($N_{0,D}$) by taking the square root of the maximum PL ($N_{0,D} \propto \sqrt{PL_{max}}$). This derived density is shown in Figure S5 over the calculated initial density. Taking EEA into account the derived density can be described as:

$$N_{0,D} = A \times N_0 - B \times N_0^2 + D\#(S1)$$

where $A$, $B$ and $D$ are constants. We add the constant $D$ to the equation to account for exciton contributions at low fluences. Auger recombination of three free charge carriers is another potential loss mechanism that can describe the losses during the funneling process:

$$N_{0,D} = A \times N_0 - C \times N_0^3 + D\#(S2)$$

where $A$, $C$ and $D$ are constants. The fits utilizing Equation S1 and S2 are shown in Figure S5a and b respectively. While both equations lead to good fits of the observed losses, the high absorption coefficient and exciton binding energy of low dimensional QWs as described in this work make the dominance of excitons after absorption more likely, with FCs only becoming dominant after the emitting QWs have been reached by the excited states. We see EEA during the funneling process therefore as the more probable loss mechanism. The constants extracted from Figure S5a are: $A_{0.8} = 7.3 \times 10^{-18}$; $A_{1.0} = 8.6 \times 10^{-18}$; $B_{0.8} = 7.4 \times 10^{-38}$; $B_{1.0} = 67 \times 10^{-38}$; $D_{0.8} = 0.52$; $D_{1.0} = 0.62$
Figure S6. Normalized PL spectra of the different perovskites using BA and NMA. All spectra were taken at the highest excitation fluences used in this work.

Figure S7. Normalized PL spectra of the different perovskites using BA and NMA. All spectra were taken at the lowest excitation fluence used in this work.

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