Supporting Information

Optoelectronic Dichotomy of Mixed Halide $CH_3NH_3Pb(Br_{1-x}Cl_x)_3$ Single Crystals: Surface versus Bulk Photoluminescence

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Determination of the halide composition of the single crystals using XRD

Vegard's law (*Eq. S1*) was used to further confirm the halide content of the crystals.

$$\alpha_{MAPbBr_{3-x}Cl_x} = (1-x)\alpha_{MAPbBr_3} + x\alpha_{MAPbCl_3} \quad (S1)$$

Where $\alpha_{MAPbBr_{3-x}Cl_x}$ is the lattice parameter of the mixed crystal, x is the compositional fraction, α_{MAPbBr_3} is the lattice parameter of the pure $MAPbBr_3$ crystal, and α_{MAPbCl_3} is the lattice parameter of the pure $MAPbCl_3$ crystal. To determine the lattice parameters, first the d-spacing (*d*) of the crystallographic planes were determined using Bragg's Law as shown in *Eq. S2* where n is the integer 1, λ is the wavelength of the Cu kα source (1.54 Å), and θ is the peak position of the (002) plane. Then, the d-spacing in combination with the miller index (*h,k,l*) is used to calculate the lattice constant for the crystal using *Eq. S3*. These values and the bromide and chloride compositional fractions are summarized in Table S1.

$$n\lambda = 2dsin\theta \quad (S2)$$

$$\alpha_{MAPbBr_{3-x}Cl_x} = \frac{d}{\sqrt{h^2+k^2+l^2}} \quad (S3)$$

Table S1. (002) peak position, d-spacing, fraction of bromide, fraction of chloride, and halide ratio.

Sample	θ / °	d / Å	α / Å	x_{Br}	x_{Cl}	Br^-:Cl^-
X = 0	30.23	2.032	4.06	1.00	0.00	1:0
X = 0.07	30.34	2.025	4.05	0.91	0.09	10:1
X = 0.11	30.40	2.021	4.04	0.86	0.14	6.2:1
X = 0.19	30.59	2.009	4.02	0.71	0.29	2.4:1
$MAPbCl_3$ [a]	31.50	1.954	3.91	0.00	1.00	0:1

[a]from Ref. 1 below

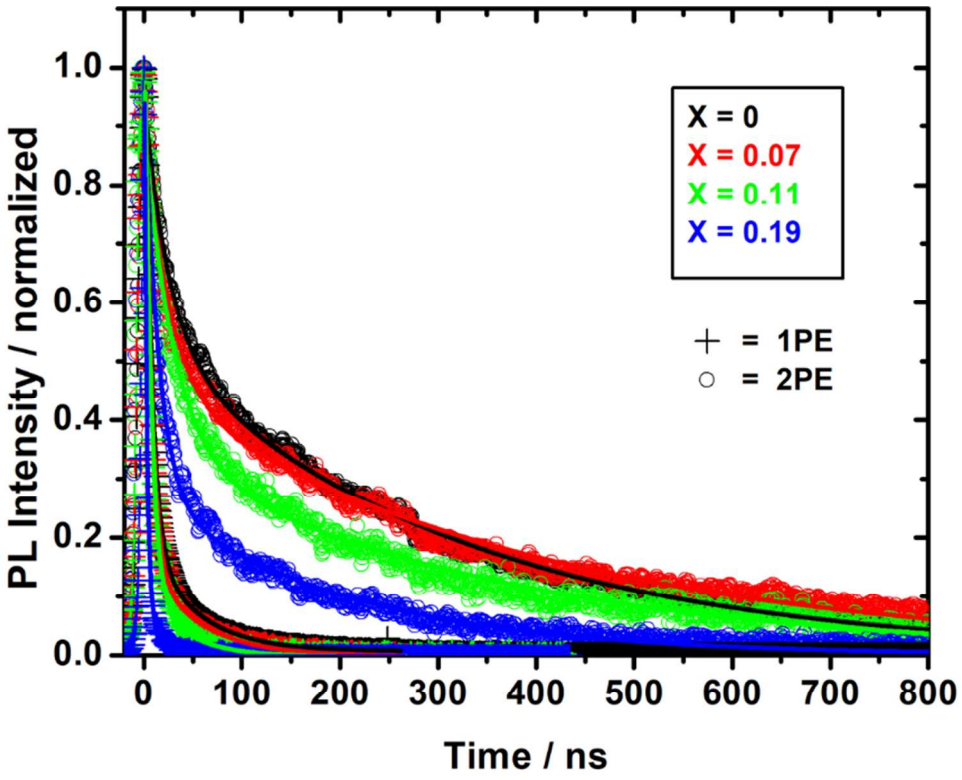

Figure S1. Extended time window of the data in Figure 6 of the main text.

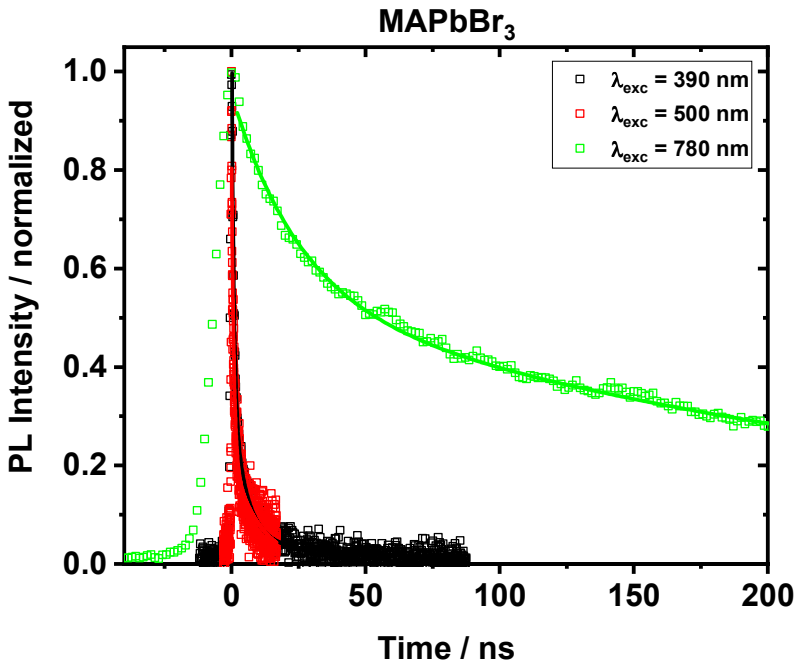

Figure S2. Comparison of TRPL decay profiles for a single crystal of $MAPbBr_3$ excited at 390, 500, and 780 nm. The shift between 2PE-780 nm and 1PE-390 & -500 nm excitation is apparent with the much longer lifetime of the 2PE decay.

Supporting Reference

1. Liu, Y.; Yang, Z.; Cui, D.; Ren, X.; Sun, J.; Liu, X.; Zhang, J.; Wei, Q.; Fan, H.; Yu, F.; Zhang, X.; Zhao, C.; Liu, S. F. *Adv. Mater.* **2015,** *27*, 5176-5183.