Electronic supplementary information for

Origin of the low-energy tail in the photoluminescence spectrum of CsPbBr₃ nanoplatelets: a femtosecond transient absorption spectroscopic study

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1. Quantum well model

The well-known quantum well model is used to fit the steady-state absorption spectrum of CsPbBr$_3$ nanoplatelets (NPLs).[1, 2] Basically, the absorbance of CsPbBr$_3$ NPLs are divided into the exciton and continuum contributions:

$$A(E) = C\alpha(E) \text{ and } \alpha(E) = X(E) + Con(E)$$

where $A(E)$ is the absorbance as a function of the photon energy, C is the scaling factor, $\alpha(E)$ is the absorption strength of the exciton, and $Con(E)$ is the absorption strength of the continuum. The $\alpha(E)$ and $Con(E)$ are respectively given by

$$X(E) = \frac{1}{2\eta}[erf(\frac{E - E_x}{W_x} - \frac{W_x}{2\eta}) + 1]\exp(\frac{W_x^2}{4\eta^2} - \frac{E - E_x}{\eta})$$

$$Con(E) = \frac{H}{2}[erf(\frac{E - E_x - E_b}{W_c}) + 1]$$

where E_x, E_b, W_x, W_c, H, and η are the exciton transition energy, exciton binding energy, exciton peak width, continuum edge width, continuum edge step height, and asymmetric broadening, respectively.

Table S1. The fitting parameters for the steady-state absorption spectrum of CsPbBr$_3$ NPLs in hexane by using the quantum well model.

Parameters	Values
E_x (eV)	2.652 ± 0.010
E_b (eV)	0.210 ± 0.020
W_x (eV)	0.048 ± 0.004
W_c (eV)	0.231 ± 0.020
H (eV^{-1})	8.873 ± 0.640
η (eV)	0.039 ± 0.003
C (eV)	0.102 ± 0.005
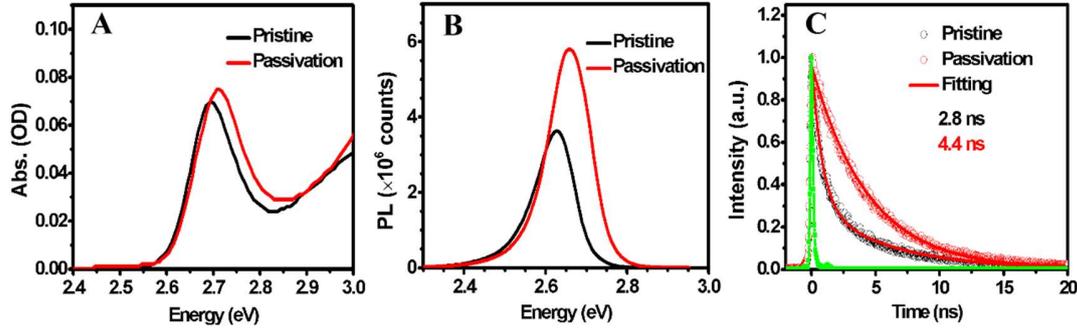
Figure S1. The steady-state absorption spectra (A) and the absorbance corrected PL spectra (B) of pristine (black line) and passivated (red line) CsPbBr$_3$ NPLs in hexane. (C) Normalized time-resolved photoluminescence decays of pristine (black circles) and passivated (blue circles) CsPbBr$_3$ NPLs in hexane. The red lines are the fits and the green line is the instrumental response function. The excitation wavelength is 403 nm and the detection wavelengths are their PL peak maxima.

The PL decay of the passivated CsPbBr$_3$ NPLs can be well fitted with a single-exponential decay function, while the PL decay of the pristine CsPbBr$_3$ NPLs needs a summation of two exponential decay functions to be well fitted. The fitting parameters for the PL decays of the pristine and passivated CsPbBr$_3$ NPLs are summarized in Table S2. Due to the limited time resolution of the TCSPC measurements (~0.2 ns), the extracted shorter time constant from the TCSPC measurement for the pristine CsPbBr$_3$ NPLs deviates somewhat from that obtained from its fs-TA spectroscopic measurement. The extracted longer time constant (τ_1) from TCSPC measurements for both pristine and passivated CsPbBr$_3$ NPLs are attributed to their exciton lifetimes. The disappearance of the shorter time constant for the PL decay of the passivated CsPbBr$_3$ NPLs also indicates that there is a small proportion of trapped exciton in the passivated CsPbBr$_3$ NPLs.

Table S2. Fitting parameters for the time-resolved PL decays of pristine and passivated CsPbBr$_3$ NPLs in hexane.

Samples	a_1	τ_1 / ns	a_2	τ_2 / ns	$<\tau>$ / ns
Pristine CsPbBr$_3$ NPLs	0.66±0.05	4.00±0.30	0.34±0.05	0.50±0.15	2.8
Passivated CsPbBr$_3$ NPLs	1.00±0.10	4.40±0.30			4.4
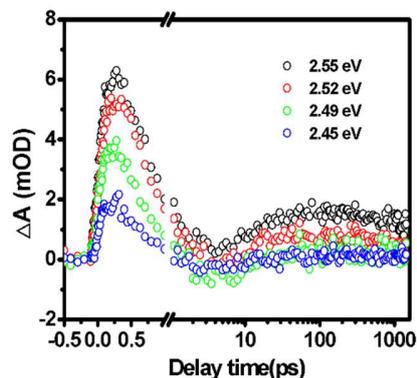
Figure S2. Femtosecond transient time profiles of CsPbBr$_3$ NPLs in hexane probed at 2.55, 2.52, 2.49 and 2.45 eV under ~3.11 eV light pump with the fluence of 1.2×10^{14} photons·cm^{-2}.
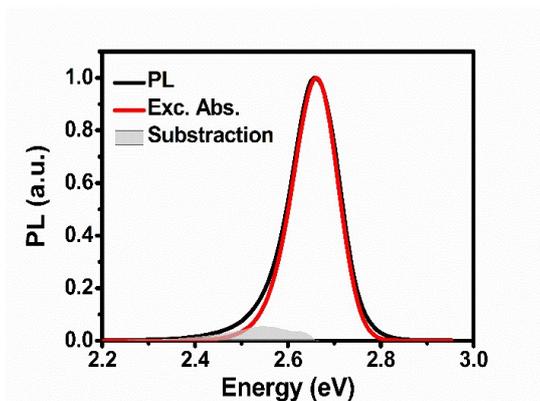
Figure S3. The PL spectrum (black line) of passivated CsPbBr$_3$ NPLs. The red line is the mirror image of the absorption spectrum of the exciton along its energy axis which keeps its maximal peak overlap with its maximal PL peak. The gray color region is the subtraction between the PL spectrum and the mirror image spectrum of the exciton absorption.

References

1. Q. Li and T. Lian, Ultrafast charge separation in two-dimensional CsPbBr$_3$ perovskite nanoplatelets. *J. Phys. Chem. Lett.*, 2019, **10**, 566-573.

2. J. Li, L. Luo, H. Huang, C. Ma, Z. Ye, J. Zeng and H. He, 2D behaviors of excitons in cesium lead halide perovskite nanoplatelets. *J. Phys. Chem. Lett.*, 2017, **8**, 1161-1168.