

Supporting information

The number of layers dependent exciton dissociation and carrier recombination in 2D Ruddlesden-Popper halide perovskites

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Material synthesis

The synthesis of $BA_2(MA)_{n-1}Pb_nI_{3n+1}$ single crystals is based on the method by Stoumpos et al.¹ with some modifications.

Synthesis of 2D BA_2PbI_4 Crystals: Lead acetate ($Pb(COO)_2$) powder (1.6g) was dissolved in 5 mL of 57% w/w aqueous hydroiodic acid (HI) solution at room temperature under constant magnetic stirring, which formed a bright yellow solution. Meanwhile, in another bottle, $n\text{-CH}_3(\text{CH}_2)_3\text{NH}_2$ (0.9 mL) was slowly neutralized with 5 mL of HI 57% w/w in an ice bath. Then, the $n\text{-CH}_3(\text{CH}_2)_3\text{NH}_3\text{I}$ solution was dropwise added to the lead solution under 100 °C and stirring, which initially produced a black precipitate, and subsequently dissolved under heating the combined solution to boiling. The stirring was then stopped, and the solution was left to cool to room temperature during which time orange plate shaped crystals can be obtained. The precipitation was deemed to be complete after about 2 h. The crystals were isolated by filtration and thoroughly dried under reduced pressure.

Synthesis of 2D $BA_2(MA)Pb_2I_7$ Crystals: Lead acetate ($Pb(COO)_2$) powder (1.6 g) was dissolved in 5 mL of 57% w/w aqueous hydroiodic acid (HI) solution at room temperature under constant magnetic stirring, which formed a bright yellow solution. Subsequent addition of solid $\text{CH}_3\text{NH}_3\text{Cl}$ (169 mg) to the hot yellow solution initially caused the precipitation of a black powder, which rapidly redissolved under stirring to afford a clear bright yellow solution. Meanwhile, in another bottle, $n\text{-CH}_3(\text{CH}_2)_3\text{NH}_2$ (0.35 mL) was slowly neutralized with 5 mL of HI 57% w/w in an ice bath. Then, the $n\text{-CH}_3(\text{CH}_2)_3\text{NH}_3\text{I}$ solution was dropwise added to the lead solution under 100°C and stirring, which initially produced a black precipitate, and subsequently dissolved under heating the combined solution to boiling. The stirring was then stopped, and the solution was left to cool to room temperature, after which cherry-red plate-shaped crystals can be obtained. The precipitation was deemed to be complete after about 2 h. The crystals were isolated by filtration and thoroughly dried under reduced pressure.

Synthesis of 2D $BA_2(MA)_2Pb_3I_{10}$ Crystals: Lead acetate ($Pb(COO)_2$) powder (1.6 g) was dissolved in 5 mL of 57% w/w aqueous hydroiodic acid (HI) solution at room temperature under constant magnetic stirring, which formed a bright yellow solution. Subsequent addition of solid $\text{CH}_3\text{NH}_3\text{Cl}$ (225 mg) to the hot yellow solution initially caused the precipitation of a black powder, which rapidly redissolved under stirring to afford a clear bright yellow solution. Meanwhile, in another bottle, $n\text{-CH}_3(\text{CH}_2)_3\text{NH}_2$ (0.16 mL) was slowly neutralized with 5 mL

of HI 57% w/w in an ice bath. Then, the $n\text{-CH}_3(\text{CH}_2)_3\text{NH}_3\text{I}$ solution was dropwise added to the lead solution under 100 °C and stirring, which initially produced a black precipitate, and subsequently dissolved under heating the combined solution to boiling. The stirring was then stopped, and the solution was left to cool to room temperature during which time deep-red plate shaped crystals can be obtained. The precipitation was deemed to be complete after about 2 h. The crystals were isolated by filtration and thoroughly dried under reduced pressure.

Sample fabrication (exfoliation)

The samples used in this investigation include $(\text{BA})_2\text{PbI}_4$, $(\text{BA})_2(\text{MA})\text{Pb}_2\text{I}_7$, and $\text{BA}_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ Ruddlesden–Popper perovskites platelets. The 2D perovskite platelets were obtained by cleaving the bulk crystals using the well-known scotch-tape method² under the protection of nitrogen. Briefly, 2D perovskite bulk crystal adhered to the scotch-tape and then flakes of perovskite crystal were peeled off from the bulk repeatedly until the platelets are thin enough to attach strongly to the Si wafer with van der Waals forces. The exfoliated $(\text{BA})_2\text{PbI}_4$, $(\text{BA})_2(\text{MA})\text{Pb}_2\text{I}_7$ and $\text{BA}_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ platelets was denoted as $n=1$, $n=2$ and $n=3$ respectively.

Characterization

Powder XRD pattern of the crystal was recorded on Bruker D8 diffractometer at a scanning rate of 1° min^{-1} , using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$).

Spectroscopic measurement

For both room temperature and low temperature measurement, steady-state photoluminescence are detected by a spectrometer (Ocean Optics, QE-Pro), and time-resolved photoluminescence measurements were performed with a time-correlated single photon counting system (PicoHarp 300, PicoQuant GmbH). A 405 nm laser diode (pulse duration 40 ps, repetition rate 20 MHz) was used as the excitation source. The perovskites samples were placed in the chamber of a close-cycled helium cryostat for the low-temperature measurements. Femtosecond pump-probe TA experiments were performed on a TA spectrometer. The laser consisted of a Ti:sapphire mode-locked oscillator that seeded a regenerative amplifier. The output of the amplifier was centered at 800 nm with a repetition rate of 1 kHz and pulse duration

of 100 fs, which was then split into pump and probe beamlines. The 400 nm pump pulses were generated by second harmonic generation using a β -BaB₂O₄ crystal. The probe beam passed through a mechanical delay stage and was used to generate a white light continuum in a 3.2 mm sapphire plate. The probe light was then detected by a polychromatic-charge coupled device. The TA measurements were performed at room temperature.

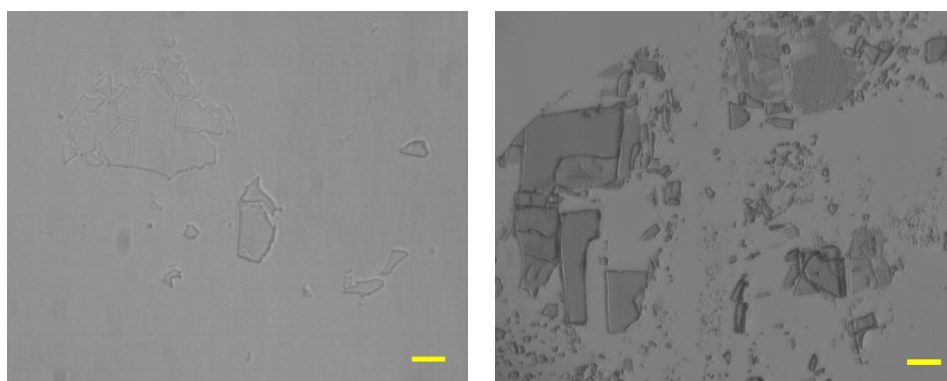


Figure S1: Typical microscopic photos for exfoliated 2D RP perovskite microplatelets (scale bar: 20 μ m)

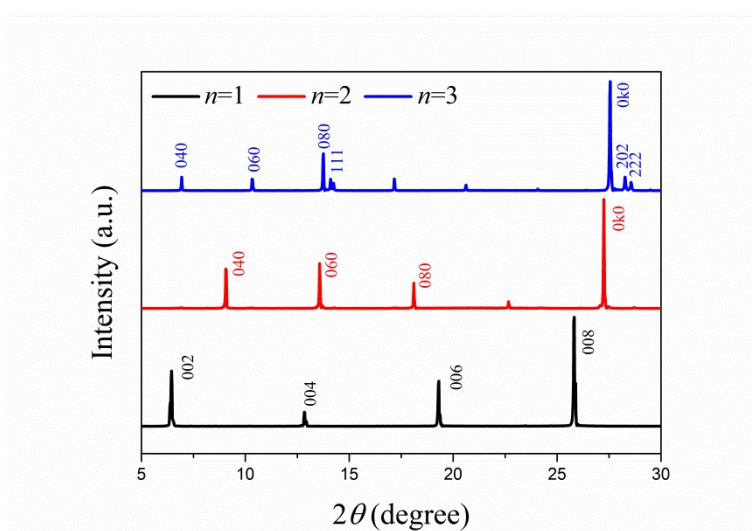


Figure S2: XRD pattern of BA₂MA_{n-1}Pb_nI_{3n+1} for n=1, 2, 3, respectively.

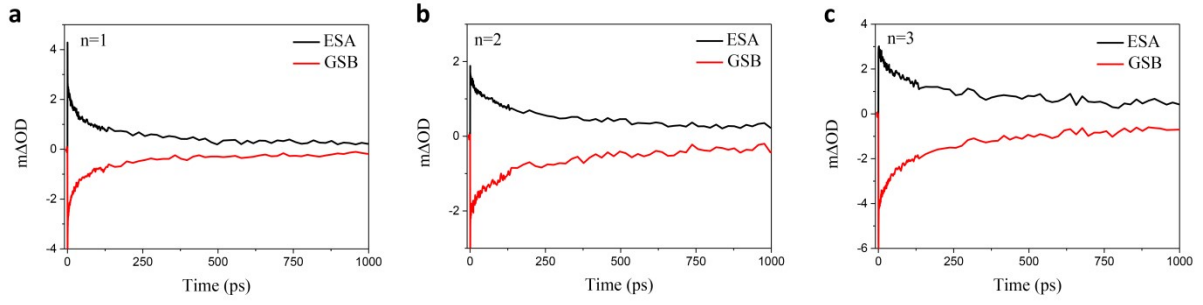


Figure S3: Transient absorption decay at ESA and GSB for (a) $n=1$, (b) $n=2$ and (c) $n=3$.

Table S1: TA decay time at bandedge wavelength extracted from bi-exponential function fitting

		τ_1 (ps)	τ_2 (ps)	τ_{eff} (ps)
$n=1$	ESA	23.5	225.0	115.8
	GSB	12.0	117.6	67.0
$n=2$	ESA	15.1	202.2	139.0
	GSB	22.7	227.1	163.6
$n=3$	ESA	30.4	268.7	170.2
	GSB	31.5	367.6	224.0

Table S2: Bi-exponential function fitting parameter for $n=1$ at room and low temperature (20 K)

	Intensity(mW/cm ²)	τ_1 (ns)	A_1	τ_2 (ns)	A_2
Room temperature	15	0.53	0.76	1.94	0.10
	50	0.50	0.64	2.08	0.11
	150	0.51	0.54	3.74	0.09
	500	0.52	0.46	3.78	0.13
Low temperature	15	0.67	0.53	1.71	0.31
	50	0.69	0.53	1.92	0.27
	150	0.63	0.83	2.13	0.25
	500	0.52	0.65	2.05	0.16

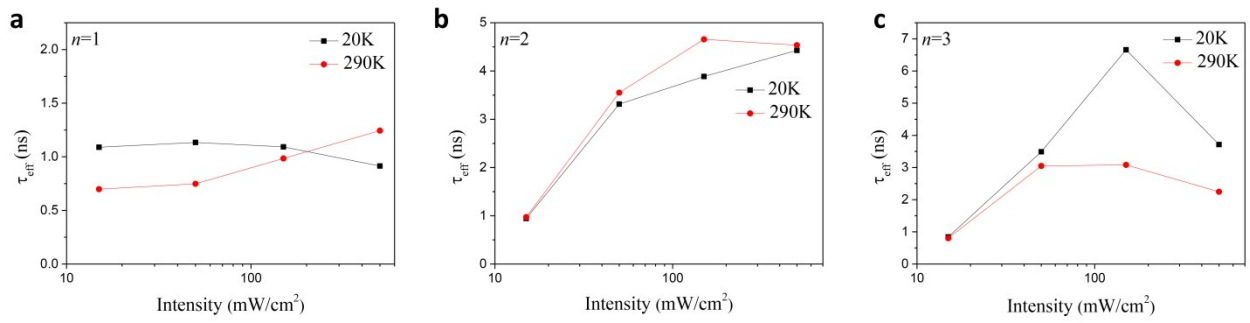


Figure S4: TRPL effective lifetime of $n=1$ (a), $n=2$ (b), $n=3$ (c) at different temperatures

References

1. Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G. *Chem. Mater.* **2016**, *28* (8), 2852-2867.
2. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306* (5696), 666-669.