Electronic Supporting Information

Efficient Interlayer Exciton Transport in Two-Dimensional Metal-Halide Perovskites.

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Sample preparation. Perovskite solutions were made following the recipes given in refs.[1–3] In short, n = 1 phenethylammonium lead iodine $(PEA)_2PbI_4$ solutions were prepared by mixing stoichiometric ratios of the precursor salts. Phenethylammonium iodide (PEAI) (Sigma Aldrich, 805904-25G) and lead(II) iodide (PbI_2) (Sigma Aldrich, 900168-5G) and were mixed with a stoichiometric ratio of 2:1 and dissolved in γ-butyrolactone (Sigma Aldrich, B103608-500G). The solution was heated to 70 °C while stirring until all the precursors were completely dissolved. The resulting solutions were kept at 70°C and the solvent was left to evaporate until reaching saturation of the solution. To obtain millimetre-sized single crystals, the saturated solutions were kept in a closed vial for about two weeks until the crystals appeared. Microscopy measurements on single crystals were performed by placing the crystal facet in contact with a cover slip using microscopy oil to avoid airgaps**.**

As an alternative to the large single crystals, smaller crystals (hundreds of micron lateral sizes) can be readily obtained using drop casting of the saturated perovskite solution on top of a microscope slide and heating to 50ºC for 2-3 hours until drying. Interlayer measurements on the drop cast samples were performed by cleaving the microscope slide and subsequent sideways placement of the cleaved microscope slide onto a cover slip. As with the large single crystals, microscope oil was used to avoid air gaps. Crystallographic orientations of both samples were confirmed by measuring the polarization orientation of photoluminescent emission (see below). All diffusion measurements presented in this manuscript were performed on the large single crystal. It is important to note though, that no significant differences in the interlayer optical and transport characteristics were observed between of the large single crystals and the drop cast crystalline phases.

X-ray diffraction measurements. X-ray diffraction (XRD) was performed with a PANanaltical X'Pert PRO operating at 45 kV and 40 mA using a copper radiation source (λ = 1.5406 Å). From Bragg's law a spacing between inorganic layers of 1.639 nm was extracted (see Fig. S1).

Absorbance and photoluminescence measurements. Absorbance spectra were obtained using a UV-Vis spectrophotometer (Mettler Toledo, UV7) on spin-coated layers of $(PEA)_2PbI_4$ (45 nm in thickness).[4] All photoluminescence measurements were performed with a sample mounted on an inverted microscope (Nikon TiU). To obtain photoluminescence spectra, samples were illuminated using a 385 nm light emitting diode (Thorlabs, M385LP1-C5). Emission spectra were recorded using an imaging spectrograph (Princeton Instruments, SpectraPro HRS-300, ProEM HS 1024BX3). Absorbance and emission spectra are consistent with literature reports for $(PEA)_2PbI_4$ and are shown in Fig. S2.[5] For the polarization analysis the same set-up was used with the addition of a linear polarizer in the light path. The linear polarizer was rotated while acquiring the emission intensity for each polarizer orientation on a camera (Princeton Instruments, ProEM HS 1024BX3). Photoluminescence lifetime measurements were performed on the same inverted microscope, using pulsed 405 nm laser excitation (PicoQuant LDH-D-C-405, PDL 800-D, 10 MHz repetition rate) at different laser fluences. The photoluminescence was collected with an APD (Micro Photon Devices PDM, 20 × 20 μm detector size). The laser and APD were synchronized using a timing board for time correlated single photon counting (Pico-Harp 300). The resulting lifetime traces are shown in Fig. S3.

Emission profile measurements. Perovskite crystals were excited with a 405 nm laser (PicoQuant LDH-D-C-405, PDL 800-D), which was focused down to a near diffraction limited spot. The laser spot images were acquired using an EMCCD camera coupled to a spectrograph (Princeton Instruments, SpectraPro HRS-300, ProEM HS 1024BX3) with a 150x magnification (NA 1.3, 100x oil immersion objective with an additional 1.5x tube lens magnification). Results are shown in Fig. 1D and S4.

Exciton diffusion measurements. Exciton diffusion measurements were performed and analysed following the same procedure as previously reported by Seitz et al.[1]

Determination of optical constants. The $(PEA)_2PbI_4$ perovskite was modelled as a layered material composed of an alternating inorganic-organic layer stack. The effective medium model to calculate the intrinsic optical constants of the organic (PEA) and inorganic (PbI_4) layers follows the method described by DeCrescent et al.[6] The organic layer was considered isotropic, non-absorbing and to have a wavelength independent

refractive index n = 1.6. The resulting constants for IP and OP components of the inorganic layer is depicted in Fig. S5.

Supplementary figures.

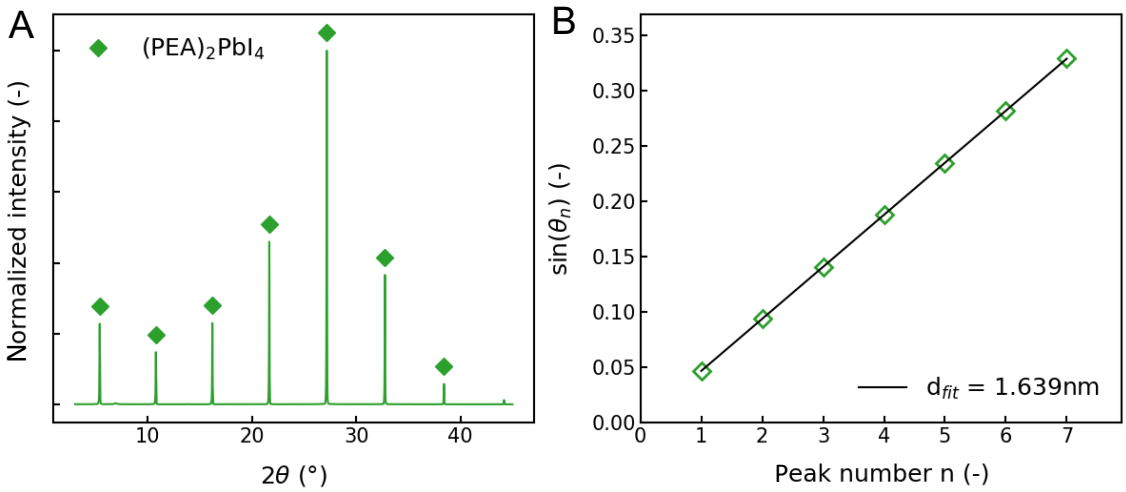

Fig S1. (a) XRD spectrum of $(PEA)_2PbI_4$. (b) Calculation of the spacing between inorganic layers d_{fit} = 1.639 nm by following Bragg's law, where θ_n is the angle of the diffraction peaks.

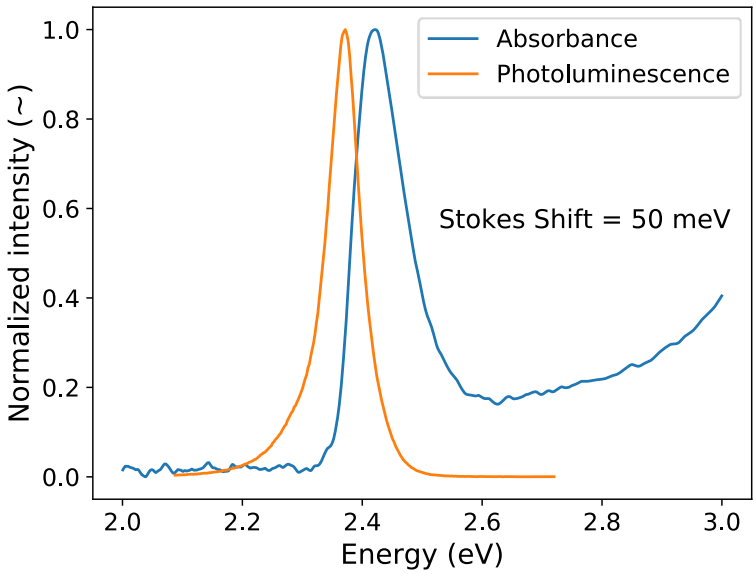

Fig S2. Absorbance and photoluminescence spectra of $(PEA)_2PbI_4$ with a Stokes Shift of 50 meV.

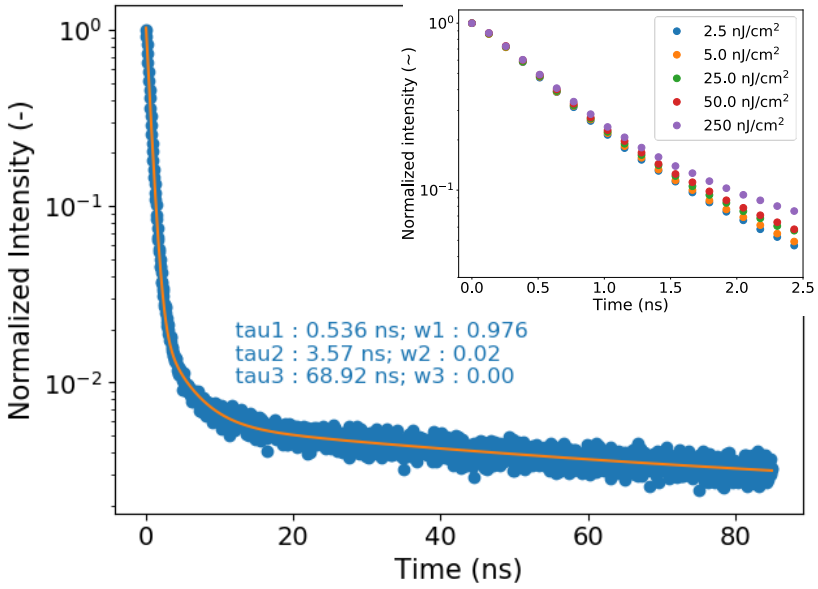

Fig S3. Photoluminescence lifetime trace of $(PEA)_2PbI_4$ with a tri-exponential fit at laser fluence of 50 nJ cm^{-2}. Fitting parameters are given in the figure. Inset: photoluminescence lifetime traces of $(PEA)_2PbI_4$ at different laser fluences taken on drop cast samples. Early timescales are unaffected by the laser fluence, demonstrating that measurements taken at 50 nJ cm^{-2} are in the single exciton regime. Small elongation of the longer lifetime components at higher fluences are due to trap state filling, as discussed in detail in ref. 1.

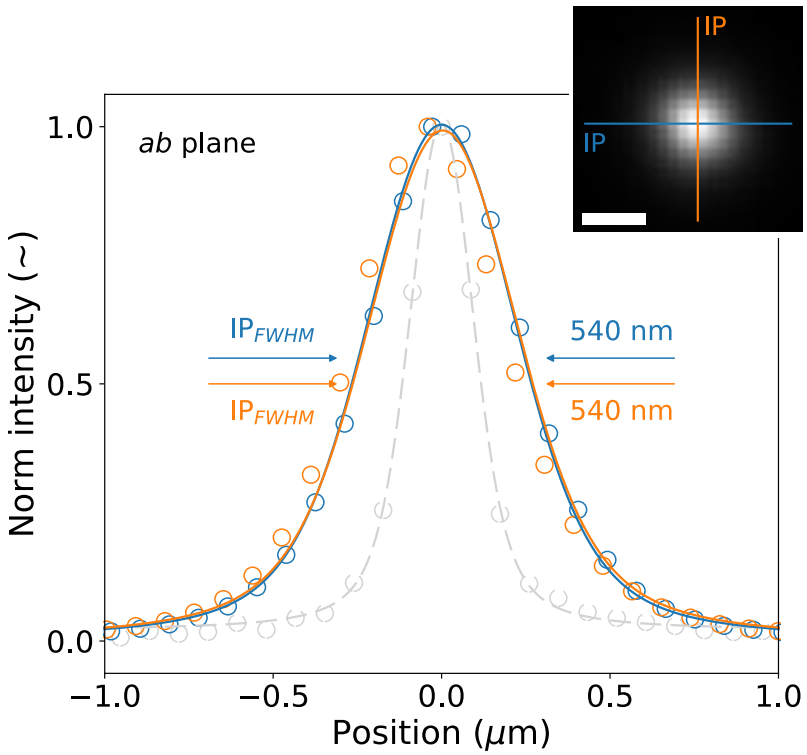

Fig S4. Emission profile along the IP (blue and orange) axes from a near-diffraction limited excitation spot on the ab plane of a $(PEA)_2PbI_4$ crystal (see inset with a scale bar of 500 nm). Dashed grey line shows the laser excitation profile.

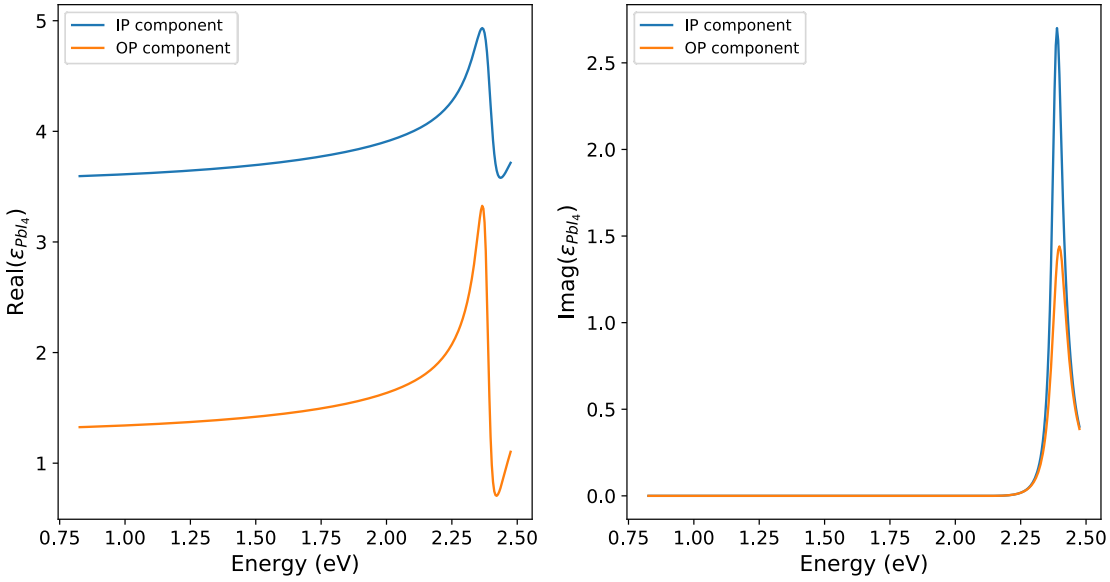

Fig S5. Intrinsic dielectric function of the PbI_4 layer of the $(PEA)_2PbI_4$ perovskite calculated using an effective medium model.[6] The real and imaginary parts of the intrinsic dielectric function are shown on the left and right panels, respectively.

References

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