

Supporting Information

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Exciton Formation Dynamics and Band-Like Free Charge-Carrier Transport in 2D Metal Halide Perovskite Semiconductors

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S1 Structural characterisation

Grazing-incidence wide-angle X-ray scattering (GIWAXS) data was acquired with a Rigaku SmartLab diffractometer. In this setup, a 3 kW Cu source (operating at 40 kV, 45 mA) with parallel beam, CBO-focused micro-area optics, and 0.5 mm length-limiting slit was incident on thin films prepared as per the Experimental section. Samples were mounted on a 2D-XRD attachment head, which incorporates a knife edge to prevent air scatter and an aligned beam stop for the direct beam. X-ray scattering was detected with a HyPix-3000 hybrid pixel-array 2D detector with a sample-to-detector distance of 65 mm. Exposed sample widths were reduced to ~4 mm to minimise sample footprint broadening due to the beam projection. Data was collected at a grazing incidence angle (α_i) of 0.5° and the detector goniometer arm was positioned at an angle of 15°. Detector images were then resampled into Q-space using scripts based on the PyFAI and pygix libraries.¹ In Figure S1, the 2D GIWAXS pattern from a FACsPbI₃ film shows the char-

acteristic Debye-Scherrer scatterings rings corresponding to reflections from a pseudo-cubic perovskite phase. As the azimuthal intensity distribution for all reflections is isotropic, the polycrystalline film has no preferred orientation, with grains randomly oriented on the substrate.



Figure S1 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) diffraction patterns measured for FACsPbI₃, showing no preferential orientation.

Figure S2 has the characteristic Bragg spots expected for a uniaxially oriented (textured) film of $(PEA)_2PbI_4$ (where PEA is phenylethylammonium), indexed with the triclinic PĪ space group.^{2,3} The scattering is consistent with a single n=1 phase, with no high dimensionality phases present in the film. The presence of intense (0*k*0) reflections in the out-of-plane direction (along Q_z) confirms the layers of the 2D material lie parallel to the substrate. Higher (0*k*0) peaks are hidden in the missing wedge, the region of scattering which is unobservable in grazing incidence geometry.



Figure S2 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) diffraction patterns measured for PEPI ($(PEA)_2PbI_4$). Bragg spots are characteristic for a single-phase film, with strong preferential orientation of the semiconductor planes parallel to the substrate.

For BAPI (Figure S3), we again observe sharp Bragg spots in the 2D GIWAXS pattern consistent with the expected reflections for the n=1 butylammonium Ruddlesden-Popper perovskite.^{4,5} Different peaks are observed in the $Q_{xy} > \pm 1$ Å⁻¹ region due to the different symmetry of this material, with BAPI indexed as a centrosymmetric orthorhombic phase at room temperature (with space group *Pbca*). We again find a single-phase film, and the scattering is dominated by a single orientation with layers aligned parallel to the substrate.



Figure S3 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) diffraction patterns measured for BAPI $((BA)_2PbI_4)$. The scattering shows a single phase is present, with strong preferential orientation of the layers parallel to the substrate.

Figures S4 and S5 show the top-view Scanning Electron Microscopy (SEM) images of PEPI and BAPI films, respectively, and show that the films are formed by homogeneous domains of several micrometre size.



Figure S4 Top-view Scanning Electron Microscopy (SEM) image of PEPI ((PEA)₂PbI₄), showing the film is formed by large homogeneous domains.



Figure S5 Top-view Scanning Electron Microscopy (SEM) image of BAPI ((BA)₂PbI₄), showing the film is formed by large homogeneous domains.

S2 Optical-Pump Terahertz-Probe (OPTP) Spectroscopy

Optical-Pump THz-Probe (OPTP) measurements were performed using a Spectra Physics Mai Tai-Empower-Spitfire Pro Ti:Sapphire regenerative amplifier. The amplifier generates 35 fs pulses centered at 800 nm and at a repetition rate of 5 kHz. The optical pump excitation was obtained by frequency doubling the fundamental laser output through a BBO crystal, resulting in 400 nm pulses. THz probe pulses were generated by a spintronic emitter which was composed of 1.8 nm of $Co_{40}Fe_{40}B_{20}$ sandwiched between 2 nm of Tungsten and 2 nm of Platinum, all supported by a quartz substrate. Detection of the THz pulses was performed using electro-optic sampling in a (110)-ZnTe crystal (thickness 1 mm). The FWHMs of the beams for the pump and THz pulses at the sample were measured to be 2 mm and 0.5 mm respectively. The sample, THz emitter and THz detector were held under vacuum ($<10^{-2}$ mbar) during the measurements. The effective charge-carrier mobility was extracted from the OPTP data using the method previously described by Wehrenfennig et al.⁶ In brief, the sheet photo-conductivity, ΔS , of a material with a thickness much shorter than the wavelength of the THz radiation can be expressed as

$$\Delta S = -\varepsilon_0 c(n_a + n_b)(\frac{\Delta T}{T}) \tag{1}$$

where *c* is the speed of light, ε_0 is the vacuum permittivity, and n_a and n_b are the THz refractive indices of the materials interfacing the perovskite layer at the front and rear respectively. The quantity $\Delta T/T$ is the ratio of the photo-induced change in THz electric field to the transmitted THz electric field in the dark. The initial number of photo-excited charge carriers *N* is given by

$$N = \phi \frac{E\lambda}{hc} (1 - R_{pump} - T_{pump})$$
⁽²⁾

with *E* being incident pump pulse energy, λ the excitation wavelength, ϕ the ratio of free charges created per photon absorbed, and R_{pump} and T_{pump} being the reflected and transmitted fractions of the pump beam. These two equations can be used to extract the charge-carrier mobility μ through

$$\mu = \frac{\Delta SA_{eff}}{Ne} \tag{3}$$

where A_{eff} is the effective area from the overlap of the pump and probe beams and e is the elementary charge. Substituting Equations 1 and 2 into Equation 3 we obtain

$$\phi\mu = -\frac{\varepsilon_0 c(n_a + n_b)(A_{eff})}{Ne\lambda(1 - R_{pump} - T_{pump})} (\frac{\Delta T}{T})$$
(4)

from which the effective charge-carrier mobility $\phi \mu$ may be determined based on the pump beam parameters and the initial measured $\Delta T/T$ of the sample. Here, μ is the charge-carrier mobility, and ϕ is the charge-to-photon branching ratio. Charge-carrier mobility values were calculated based on the average of at least 10 measurements.

OPTP photoconductivity spectra

The effective photoconductivity $\Delta \sigma(\omega)$ is normally calculated from the pump-induced changes to the THz transmission by:

$$\sigma_{photo}(\omega) = -\frac{\varepsilon_0 c(n_1 + n_2)}{L} \frac{\Delta T}{T}$$
(5)

where *L* is the semiconductor film thickness. This formula is valid when the THz transmission of the semiconductor in the dark is approximately equal to the transmission of the substrate. However, this approximation is not valid for THz frequencies near phonon resonances, as has been demonstrated by La-o-vorakiat et al.,⁷ or for highly doped semiconductor films, as demonstrated by Ulatowski et al.⁸ A more accurate approach for calculating σ from the experimental data takes into account the dark THz spectrum in the following equation:

$$\sigma_{photo}(\omega) = -\frac{T_{substrate}}{T} \frac{\varepsilon_0 c(n_1 + n_2)}{L} \frac{\Delta T}{T + \Delta T}$$
(6)

where $T_{substrate}$ is the substrate transmission and T is the transmission of the sample (substrate and semiconductor) in dark. The approximation $\frac{\Delta T}{T+\Delta T} = \frac{\Delta T}{T}$ is still valid when $\Delta T \ll T$, such as in the cases presented in this study. However, the additional term $\frac{T_{substrate}}{T}$ results in significant corrections to the phonon features superimposed in the photoexcited spectra.

S3 Optical absorption spectra

Elliott's theory describes the effect of excitons to the optical absorption of semiconductors.⁹ For a 2D semiconductor such as the Ruddlesden-Popper perovskites investigated here, the total absorption coefficient α as a function of incident energy *E* is given by¹⁰:

$$\begin{aligned} \alpha(E) &= A_0 \left[\sum_{n=1}^{\infty} \frac{4E_0}{(n-1/2)^3} \operatorname{sech}\left(\frac{E - E_G + \frac{E_0}{(n-1/2)^2}}{\Gamma}\right) \right. \\ &+ \int_{E_G}^{\infty} \operatorname{sech}\left(\frac{E - \varepsilon}{\Gamma}\right) \frac{2}{1 + \exp\left(-2\pi\sqrt{\frac{E_0}{E - E_G}}\right)} \times \frac{1}{1 - (8\alpha m^*/\hbar^4)(\varepsilon - E_G)} d\varepsilon \right] \end{aligned} \tag{7}$$

where the pre-factor A_0 is proportional to the transition dipole moment, E_G is the bandgap, m^* is the effective mass, $E_b = E_0/(n-1/2)^2$ is the exciton binding energy, where n = 1, 2, 3... is an integer. The broadening parameter Γ was considered to be the same for the excitons and band-to-band continuum, for simplicity.



Figure S6 Absorption spectra of PEPI ((PEA)₂PbI₄, left) and BAPI ((BA)₂PbI₄, right) at 295K. Shaded areas show the continuum (blue, with Coulomb enhancement) and exciton contributions (orange) to the fit to the Elliott formula (orange line).

Figure S6 shows the absorption spectra and Elliott fits for PEPI ((PEA)₂PbI₄, left) and BAPI ((BA)₂PbI₄, right) at room temperature. We note the low quality of the fits for BAPI, which is likely associated with higher levels of disorder and scatter in the thin-film material compared to PEPI.



Figure S7 Absorption spectrum of PEPI ((PEA)₂PbI₄) at 10K. Shaded areas show the continuum (blue, with Coulomb enhancement) and exciton contributions (orange) from the fit to the Elliott formula (orange line). The formula has been modified to include multiple exciton resonances as described by Neutzner et al.¹⁰)

The low temperature (10K) spectrum for PEPI shows multiple sharp exciton peaks, which can be described by equally distanced resonances as described by Neutzner et al.¹⁰ In the case of BAPI, the phase mixtures at low temperature complicate the analysis of the spectrum. Figure S8 shows the spectra of thick films of PEPI and BAPI where the continuum onset can be more clearly observed, although the exciton fine structure is hidden by the saturation of the transmission.



Figure S8 Absorption spectrum of thicker (600 nm) films of PEPI ((PEA)₂PbI₄) and BAPI ((BA)₂PbI₄) at 4K. The exciton fine structure cannot be resolved owing to saturation of the transmission signal, however, the continuum onset can be clearly seen. The approximate energy distance between the continuum and exciton is highlighted for each sample and represents the exciton binding energy.

S4 Modelling of the excitonic resonances in the THz region



Figure S9 Modelled OPTP photoinduced THz conductivity spectrum assuming excitonic resonances with binding energy 100 meV, calculated as described by Davies et al.¹¹ Both figures show the same spectrum, displayed over different ranges.

S5 Dielectric function and Lyddane-Sachs-Teller relation

The Lyddane-Sachs-Teller relation defines the relative energies of the transverse optical (TO) and longitudinal optical (LO) phonon according to the ratio of the static (ε_{st}) and high-frequency (ε_{∞}) values of the dielectric function:¹²

$$\frac{(E_{LO})^2}{(E_{TO})^2} = \frac{\varepsilon_{st}}{\varepsilon_{\infty}}$$
(8)



Figure S10 Visible-to-near-infrared transmission and reflection spectra of PEPI ((PEA)₂PbI₄) and BAPI ((BA)₂PbI₄).

We can calculate ε_{∞} as the square of the refractive index, which we obtain from the reflectivity of the semiconductor in the near-infrared (Figure S10), where the absorption coefficient is negligible.

The static permittivity ε_{st} was obtained from the complex transmission spectrum in the THz region in dark. The transmission function $T(\omega) = \frac{T_{sample}}{T_{substrate}}$ as a function of the angular frequency ω relates to the complex refractive index of the semiconductor film \tilde{n} according to

$$T(\boldsymbol{\omega}) = \frac{(1+\tilde{n}_s)}{(1+\tilde{n}_s) - i(\tilde{n}^2 + \tilde{n}_s)\boldsymbol{\omega}d/c}$$
(9)

where \tilde{n}_s is the substrate refractive index, and *d* is the thickness of the film. We obtained ε_{∞} from the reflectivity spectra of PEPI and BAPI taking into account the presence of Fabry-Perot interference in the spectra, that are calculated based on the film thickness.



Figure S11 Complex dielectric function of PEPI ((PEA)₂PbI₄, left) and BAPI ((BA)₂PbI₄, right) measured by time domain THz spectroscopy.

The complex dielectric function $\varepsilon = \varepsilon' + i\varepsilon''$ can be determined from the experimental THz transmission spectra by substituting $\tilde{n}^2 = \varepsilon$. Figure S11 shows the complex dielectric function measured by timedomain THz spectroscopy on thin films of PEPI and BAPI. The spectra were fit considering one Lorentzian oscillator corresponding to a dominant TO phonon mode according to:

$$\varepsilon_n(\omega) = A_n \frac{\omega_n^2}{\omega_n^2 - \omega^2 - i\omega\gamma_n}$$
(10)

where A_n is the amplitude of the contribution of the mode, which is proportional to the oscillator strength. ω_n is the resonance frequency and γ_n is the damping constant.

Employing the values obtained for ε_{∞} and ε_{st} in Equation 8, we calculate E_{LO} for PEPI and BAPI. The values obtained are listed in Table S1.

	PEPI	BAPI
ε_{∞} (from NIR reflectivity)	3.5	3.5
ε_{st} (from THz spectroscopy)	7.3	7.8
E_{TO} (from THz spectroscopy)	8.2 meV	7.6 meV
E_{LO} (from Equation 8)	11.8 meV	11.3 meV

Table S1 Dielectric constants and phonon energies for PEPI ((PEA)₂PbI₄) and BAPI ((BA)₂PbI₄).

Given uncertainties in the determination of ε_{∞} and ε_{st} that are associated with scattering, substrate thickness, and sample thickness, the values obtained for PEPI and BAPI are virtually equivalent. The dominant factor resulting in different calculated energies for the LO phonon modes are the energies of the TO phonon modes determined by THz spectroscopy.

S6 Analysis of temperature dependence of photoluminescence FWHM

The scattering between charge carriers and phonons or impurities result in broadening of the photoluminescence (PL) linewidth. A detailed analysis of temperature-dependent PL broadening has been previously reported by Wright et al.¹³

Briefly, the variation of the broadening Γ as a function of temperature in most inorganic semiconductors can be described as:

$$\Gamma(T) = \Gamma_0 + \Gamma_{ac} + \Gamma_{LO} + \Gamma_{imp} = \Gamma_0 + \gamma_{ac}T + \gamma_{LO}N_{LO}(T) + \gamma_{imp}e^{-E_{ib}/k_BT}$$
(11)

where Γ_0 is the temperature-independent inhomogeneous broadening term, associated with static disorder. Γ_{ac} is a homogeneous broadening term associated with acoustic phonon scattering, generally assumed to follow a linear temperature dependence according to coupling strength γ_{ac} as acoustic phonon energies tend to be small compared to thermal energies over the investigation range. Γ_{LO} is the homogeneous broadening term associated with longitudinal optical (LO) phonon (Fröhlich) scattering, defined by the coupling strength γ_{LO} and the Bose-Einstein distribution function of phonon occupation given by $N_{LO}(T) = 1/(e^{E_{LO}/k_N T} - 1)$, where E_{LO} is the energy of the LO phonon. Γ_{imp} phenomenologically accounts for scattering from ionized impurities with an average binding energy E_{ib} .

In this work, we have extracted the full-width-at-half-maximum (FWHM) from the PL spectra by fitting with a combination of Lorentzian peaks to account for the multiple components. Only the broadening of the decomposed main band-edge emission peak (B2 in BAPI and P2 in PEPI, as highlighted in the main text) has been used for the analysis.

From the THz absorption spectra we measure the transverse optical (TO) phonon modes, from which we derive the corresponding LO phonon frequencies using the Lyddane-Sachs-Teller (LST) relation between the static and high-frequency values of the dielectric function¹⁴ (see Section S5). From the frequency of the pronounced TO phonon mode observed in the THz absorption spectra of PEPI and BAPI and the LST relation, we obtain $E_{LO}=11.8$ meV for PEPI and $E_{LO}=11.3$ meV for BAPI. We employ these values as fixed parameters in fits to the FWHM of the PL based on a Bose-Einstein term to capture the temperature dependence¹³ (see Section S6 in SI for details) and obtain coupling strengths of $\gamma_{LO}=24.7$ meV for PEPI and $\gamma_{LO}=31.6$ meV for BAPI, indicating stronger coupling of charge carriers to optical phonon modes of the polar lead iodide lattice for BAPI.

S7 Transient Absorption Analysis

Transient Absorption spectra were fitted following a previously reported methodology.¹⁵ For the 3D perovskite FACsPbI₃, the continuum contribution was fitted according to the Boltzmann distribution of band filling, reproducing the high-energy tail of the photobleach. Figure S12 shows samples of the fitted spectra and the evolution of the high-energy distribution during cooling. The extracted charge-carrier temperature over time is shown in Figure S13, however, we note that the cooling timescales are convoluted with the temporal resolution of the experiment.



Figure S12 Normalised Transient Absorption spectra of a FACsPbI₃ thin film, recorded at different time delays after 3.1-eV photoexcitation, showing the charge-carrier cooling dynamics. Dots are experimental data and solid lines are fits.



Figure S13 Charge-carrier temperature extracted from the fits to the TA spectra of a FACsPbI₃ thin film according to the Boltzmann distribution, compared with the dynamics of the subgap PIA area.

In the present work, for 2D perovskites, we do not observe significant contribution of band filling photobleach, and we find that the TA lineshape of PEPI and BAPI can be successfully described by the exciton contribution in combination with a photoinduced absorption that we assign to bandgap renormalisation. The exciton contribution is described by a reduction in the oscillator strength that induces a photobleach, combined with lineshape broadening and a shift in the resonance frequency. The shift of the exciton peak is a result of the bandgap renormalisation and variations to the exciton binding energy associated with screening effects.¹⁶ We choose to fit the exciton shift individually, because our experimental data does not allow for very precise fit of the bandgap renormalisation and continuum contribution.



Figure S14 Transient Absorption spectra of PEPI ((PEA)₂PbI₄), BAPI ((BA)₂PbI₄), and FACsPbI₃ at different time delays after 3.1-eV photoexcitation. Dots are experimental data and solid lines are fits. The shaded area illustrates the subgap PIA, the dynamics of which has been demonstrated to correlate with charge-carrier cooling.



Figure S15 Normalised Transient Absorption spectra of PEPI ((PEA)₂PbI₄), BAPI ((BA)₂PbI₄), and FACsPbI₃ at different time delays after 3.1-eV photoexcitation, showing negligible changes to lineshape after thermal relaxation. Dots are experimental data and solid lines are fits.

Figure S14 shows samples of the TA spectra for PEPI, BAPI, and FACsPbI₃. The dynamics of the photobleach shown in Figure 4 of the main text is taken as the variation in exciton absorption amplitude. Charge-carrier cooling dynamics are often evaluated by fitting the high-energy side of the TA photobleach signal to a Boltzmann distribution.^{15,17} However, this approach is not particularly valid in these 2D semiconductors, where the exciton binding energies of hundreds of meV would result in a large separation between the excitonic photobleach and the edge of the continuum, and where we expect excitons to dominate the TA spectra at the optical band-edge. Alternatively, the subgap photoinduced absorption (PIA) observed in the low-energy side of the spectra has been demonstrated to correlate reasonably well with the cooling dynamics,¹⁷ as shown in Figure S13. This PIA is a result of changes to the exciton absorption lineshape, likely from more than one contribution including broadening and shifts. For simplicity, we take the area of the subgap PIA (illustrated by the shaded area in Figure S14) as a qualitative analysis of thermal relaxation dynamics.

Figure S15 shows the normalised TA spectra at longer time delays, demonstrating how the lineshape of the spectra remains largely unchanged after thermal relaxation.

S8 Charge-carrier recombination dynamics



Figure S16 OPTP photoconductivity transients obtained with various intensities of 3.1-eV photoexcitation of PEPI ((PEA)₂PbI₄), BAPI ((BA)₂PbI₄) at 4K and 295K. Insets show the normalised dynamics of each panel, in log Y scale, with superimposed modelled curves of bimolecular recombination kinetics. The legend indicating the excitation fluences applies to all panels.

The tails of the OPTP transients extend over hundreds of picoseconds and show a distinctively bimolecular character, which is more clearly appreciated in the OPTP transients normalised to the maximum amplitude and plotted in log scale, as shown in the insets of Figure S16. To characterise such second-order dynamics, the tails of the transients from 5 ps to 400 ps were fitted with a second-order decay rate as $\frac{dn}{dt} = k_2 \phi n_0^2$. The global fit of the fluence-dependent transients obtained for PEPI and BAPI at 4K and 295K are shown as solid lines in the insets of Figure S16. The fitted rates are listed in Table S2.

Table S2 Effective electron-hole sum mobilities $\phi\mu$ and bimolecular recombination rate constants ϕk_2 for PEPI ((PEA)₂PbI₄) and BAPI ((BA)₂PbI₄) at 296 K and 4 K.

	Т	PEPI	BAPI
$\phi\mu (cm^2 V^{-1} s^{-1})$	295K	$7.6{\pm}0.1$	$3.4{\pm}0.1$
$\phi \mu \ (cm^2 V^{-1} s^{-1})$	4K	$48.8{\pm}0.7$	$14.1 {\pm} 0.5$
$\phi k_2 \ (cm^3 s^{-1})$	295K	$6.5 imes 10^{-9}$	$3.1{ imes}10^{-9}$
$\phi k_2 \ (cm^3 s^{-1})$	4K	9.9×10^{-9}	11×10^{-9}



Figure S17 Time-resolved photoluminescence (PL) spectra for thin films of PEPI ((PEA)₂PbI₄) and BAPI ((BA)₂PbI₄), collected at different time delays after excitation by time-resolved PL upconversion spectroscopy. The origin at t=0ps has been defined at the maximum of the PL transient, so the spectra at -0.3 ps is taken at the rise of the signal. The early-time spectrum shows a high-energy shoulder associated with hot-carrier emission, but such feature is only observed during the rise time of the PL signal. Following fast cooling dynamics, no significant changes to the PL lineshape are observed.



Figure S18 PL transients for thin films of PEPI ((PEA)₂PbI₄) and BAPI ((BA)₂PbI₄), collected by time-resolved PL upconversion spectroscopy, measured at the peak of the emission spectra for different excitation fluences. The origin t=0ps has been defined at the maximum of the PL transient.



Figure S19 Transient absorption dynamics measured at the band-edge photobleach energy for thin films of PEPI ((PEA)₂PbI₄) and BAPI ((BA)₂PbI₄), superimposed with the OPTP transients (boundary of shaded area) that has been acquired simultaneously. The orange line shows the square root of PL transients obtained by PL upconversion spectroscopy at 0.8 μ J/cm² excitation with 3.02-eV pulses.



Figure S20 Transient absorption dynamics measured at the band-edge photobleach energy of FACsPbI₃, superimposed with the OPTP transients (boundary of shaded area) acquired simultaneously, for excitation fluence of 19 μ J/cm² with photon energy of 3.1 eV.



Figure S21 Instrument response function (IRF) fitted as a Gaussian to the OPTP photoconductivity data of FACsPbI₃ with 800 nm photoexcitation (at the band-edge, thus with negligible associated cooling dynamics).



Figure S22 Instrument response function (IRF) fitted as a Gaussian to the TA data of PEPI probed at 500 nm, with 400 nm photoexcitation.



Figure S23 OPTP transient (normalised) of PEPI at room temperature, with 3.1 eV photoexcitation at 10 μ J/cm² incident from the film side (front) or the substrate side.

S9 Calculation of photoexcitation density in the 2D perovskite layers

To calculate the photoexcitation density in a sheet of 2D semiconductor, the values of the thickness of a single layer d_i (i.e. the distance between the top of the lead-halide octahedra of subsequent semiconducting layers) were obtained from reported structure in the literature.¹⁸ We used $d_i = 1.6$ nm for (PEA)₂PbI₄ and 1.4 nm for BAPI. The thickness of the films was measured using a Dektak 150 surface profilometer. The film thickness was divided by the thickness of each layer and the photoexcitation densities in each layer across the film were calculated according to the Lambert-Beer absorption profile. The density used for applying the Saha equation and obtaining the values plotted in Figure 5 of the main text was the weighted average of the densities across the film profile.

S10 Analysis of exciton and free-carrier relative populations

The formalism most commonly employed to model the exciton and free charge-carrier populations in semiconductors is the Saha equation, ^{19,20} which gives the equilibrium branching ratio $\alpha = n_{free}/n_0$, i.e. the fraction of free-carrier density n_{free} out of the total density of electron-hole pairs $n_0 = n_{free} + n_{ex}$ where n_{ex} is the exciton density, according to

$$\frac{\alpha^2}{1-\alpha} = \frac{1}{n_0(h/\sqrt{2\pi m^* k_B T})^d} exp(\frac{-E_B}{k_B T})$$
(12)

where *d* is the semiconductor dimension, *T* is the temperature, and m^* is the electron-hole reduced mass. Our analysis assumes that α can be estimated as $\Delta S_0 / \Delta S_{5ps}$, where the photoconductivity signal at t=0 (ΔS_0) reflects the total density of electron-hole pairs in the system, before and after equilibrium has been reached, while the photoconductivity signal after the initial fast decay (ΔS_{5ps}), taken at t = 5 ps, is associates with the density of free carriers n_{free} remaining at equilibrium.

We draw attention to the following factors that may lead to inaccuracies in this analysis: firstly, while unexpected, it is possible that excitons exist within the very first picosecond following photoexcitation, either by direct photogeneration or rapid formation. Secondly, the mobility of charge-carriers may change rapidly during the cooling process within the first picosecond following photoexcitation. Both such scenarios would result in an underestimation of the total population of charge-carrier pairs present from the initial ΔS_0 signal, and consequently an overestimation of α .

While we acknowledge that these inaccuracies hinder a precise quantitative analysis of the estimated α from $\Delta S_0/\Delta S_{5ps}$, we maintain that our results and analysis are reliable from a qualitative perspective, because the two possibilities above are insufficiently significant to account for the discrepancies between the experimental and theoretical estimates of α , in particular at low temperatures, as explained below.

Based on the high exciton binding energies of the 2D perovskites studied in our work, the Saha equation predicts essentially non-existent free electron-hole populations at lower temperatures (e.g. $\alpha \sim 10^{-127}$ at 4K for the exciton binding energy of 200 meV). The experimental determination, however, results a factor of ~0.2 (see Figure 5 of the main manuscript). In order to determine the accuracy with which we know that the experimentally determined value is indeed non-zero, we determine the extent to which the noise level influences the experimental values. To approximate the experimentally estimated α at 4K to the noise level (calculated as the standard deviation of the measurement and shown by the error bars in the plots in Figure 5d in the main text), we would need to consider an overestimation by a factor of ~10 in BAPI and up to ~30 in PEPI, which is highly unlikely to be the case.

We note in particular, that such effects would equally affect the photon-to-free-charge-branching ratio ϕ , which is essentially identical to the fraction of initially generated free charge-carriers, given that every absorbed photon generates either an exciton or a free charge carrier. Therefore, a potential severe underestimation by a factor of ~30 of the fraction free charge carriers initially generated, while allowing agreement with Saha within experimental boundaries (see Note S10 in SI), would then also lead to an elevation of the derived electron-hole sum mobilities μ by the same amount. In this case, values of μ derived from $\phi\mu$ (around 50 cm²/(Vs), as evident in Figure 3a of the main manuscript) would exceed 1500 cm²/Vs at 4K, higher by an order of magnitude than those typically recorded^{11,21} for corresponding 3D lead iodide perovskites. It is very unlikely that the low-dimensional RP perovskite would present charge-carrier mobilities an order of magnitude higher than their 3D counterparts.

In summary, the significant deviations from Saha that we observe in our experiments cannot easily be explained by inaccuracies of the determination of the total density of charge-carrier pairs from ΔS_0 .

It is worth noting that while we assume a situation of quasi-equilibrium after few picoseconds following

photoexcitation, one must also consider that our experiments do not necessarily represent accurately the steady-state equilibrium conditions. However, even if we consider that excitons simply take longer to form in 2D RP perovskites, the timescales of hundreds of picoseconds we report here even at 4K are surprisingly long and demonstrate how the efficient transport of free charge carriers can be harnessed from these versatile low-dimensional materials.

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