Supporting Information for
"Nanoscale-resolved surface-to-bulk electron transport in CsPbBr$_3$ perovskite"

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1 Materials and Methods

1.1 TR-APRES measurements

The ultrashort extreme ultraviolet probe pulses were generated at the Harmonium light source by means of high harmonic generation. Pump pulses at an energy of $\sim 3.2$ eV were used to promote valence electrons into the unoccupied conduction band (CB) across the bandgap. The ARPES spectra were collected by a hemispherical electron analyser (Specs Phoibos 150). To achieve the temporal resolution of $\sim 70$ fs (see SI), a time-delay compensated monochromator, tunable in the energy range of 15 – 50 eV, was employed, providing an overall energy resolution < 300 meV (see below).

1.2 Sample preparation

Single crystals were grown from a liquid solution using an inverse temperature crystallization method. At room temperature, according to X-ray diffraction, the crystal cell of CsPbBr$_3$ possesses an orthorhombic symmetry originating from a distortion of an ideal cubic cell through a rotation of the [PbBr]$_4^-$ octahedra, surrounding the central Cs$^+$ cation. The samples were mechanically cleaved under ultrahigh vacuum (UHV) conditions, which yielded a flat fresh surface, free of contamination.

1.3 Surface band banding

The sample surface appears to be moderately $n$-doped, which manifests itself in a typical downward band bending of $\sim 300$ meV. Donor-like surface states could originate from reduced lead and/or from bromide deficiency at the surface. Illumination by a continuous wave white light source with $\sim 1$ mW/cm$^2$ of irradiance was used to saturate the surface photovoltage (see below), and, therefore, to ensure flat band conditions during measurements.
2 Supplementary text

2.1 Estimation of the temporal and the energy resolution of the TR-ARPES setup

The time resolution of the TR-ARPES setup was characterized by following the ultrafast broadening of the valence band (VB) of WSe$_2$ upon photoexcitation. The effect is caused by a change in hole lifetime, and it has a rise time of a few fs, one order of magnitude smaller than the temporal resolution of the setup. The broadening as a function of time was fitted with a model obtained by convoluting a Gaussian with a decaying exponential, as shown in Fig. S1. The full width at half of the maximum (FWHM) of the Gaussian represents a good estimate of the temporal resolution, defined as the cross-correlation between the pump and the probe pulses, yielding a value of $\sim 70$ fs.

The energy resolution was estimated from the FWHM of the Gaussian fit of an energy distribution curve (EDC). This approach is justified by the fact that the natural VB width of WSe$_2$ is an order of magnitude smaller than the energy resolution, yielding a value of $\sim 300$ eV, as shown in Fig. S2. This should be regarded as an upper boundary, since the WSe$_2$ sample surface quality can significantly contribute to this value.

2.2 Ab-initio calculation of the electronic band structure

Figure S3 shows the calculated electronic band structure of CsPbBr$_3$ in cubic high temperature phase at different levels of theory, ranging from density functional theory (DFT) using either a semi-local (PBE) or a hybrid (HSE) functional approximation, to Green’s function theory ($G_0W_0$), as denoted in the legend. Even though $ab$ initio calculation predicts the CB and VB extrema to be located at the center of the Brillouin zone (BZ) in the room temperature orthorhombic phase, recent ARPES band mapping study$^5$ reveals that upon distortion only a negligible spectral weight transfer occurs towards the BZ center, and the bandgap extrema are located at the corners ($\bar{M}$) of the surface-projected BZ (SBZ), mo-
momentum regions only accessible by extreme ultraviolet (EUV) photon energies. It is worth noting that the surface cleave typically reveals the (001) face of the crystal.\textsuperscript{8}

During a tri-molecular Auger recombination (AR) event an electron and a hole recombine and transfer the released energy to a third body, which can be an electron in case of a so-called $eeh$ process, or a hole in case of a $hhe$ process.\textsuperscript{9} The probability of such an event is greatly enhanced when the third particle has an available final state higher in the CB or lower in the VB, respectively. The vertical arrows at the R point in Fig. S3 indicate the magnitude of an excitation of the third electron or hole in the case of an electron and a hole recombining across the bandgap. The color of the arrow corresponds to the color of the respective level of theory in the legend of Fig. S3. This analysis reveals that a hole excited in the VB will have an available final state. Conversely, the electron in the CB would require an additional phonon to satisfy the energy and momentum conservation in such a process. Therefore, we expect the $hhe$ process to dominant channel of AR in CsPbBr$_3$.

2.3 Optical sample characterization

Figure S4 shows the absorption and the photoluminescence spectra of the crystals. Linear extrapolation of the absorption edge yields the value of the optical bandgap of $E_{\text{gap}} = 2.29$ eV, as displayed in the inset.

2.4 Surface defects and band bending

Upon sample cleavage, it was observed that the measured valence band kinetic energy depends on several factors, such as the EUV flux and the sample illumination condition in the experimental chamber. These electrostatic effects can evolve with time and depend on the sample history and vary spatially on the cleaved surface. Previous studies have discussed similar effects in ultraviolet photoelectron spectroscopy of lead halide perovskite (LHP) semiconductors.\textsuperscript{7,10} In particular the presence of surface states and defects induces a band bending effect at the surface of hybrid LHPs. Sample illumination by visible radiation
can counteract this effect, by producing electron and holes which can restore flat band conditions.\textsuperscript{10} Past literature on LHPs have correlated the band bending effects to the presence of reduced lead species on the surface, observed with core level spectroscopy, and possibly indicating vacancies of Br ions. Mobile Br ions were also reported in ionic conductivity studies on CsPbBr\textsubscript{3}.\textsuperscript{11} The surface defects act as electron donors, as confirmed by studies of deposition of electron acceptor molecules,\textsuperscript{7} and induce a downward band bending, i.e. reduce the measured kinetic energy of the surface bands. The surface density of defects was found to increase as a function of time with illumination in hybrid LHPs. Such light-induced modification (observed under UHV conditions) is potentially linked to the stability problems of LHP solar cells.

To monitor quantitatively band bending effects and defect formation on the surface, we measured Pb 5d core states, readily accessible by 40 eV photons. A typical spectrum is shown in Fig. S5 (a), the lineshape is dominated by Gaussian broadening at room temperature and by the experimental resolution, and can be fitted using a simple Gaussian function and a Shirley background. On the high kinetic energy side of the doublet, a minority component may develop during experiments (peak C), which is associated with surface defects. The band bending at the surface was studied by comparing the highest kinetic energy peak of the doublet Pb (5d\textsubscript{5/2}) in dark and under illumination by either a continuous-wave (CW) white light LED, by the fs UV pump laser, or by a CW 405 nm UV laser diode. Upon illumination with any of the light sources the 5d\textsubscript{5/2} level shifts to higher kinetic energy, indicating downward band bending, similar to previous reports for LHPs.\textsuperscript{6} The shift as a function of radiant intensity is illustrated in Fig. S5 (b), for the case of the fs pump laser. The shift saturates at a corresponding average intensity of a few mW/cm\textsuperscript{2}, indicating the recovery of flat band conditions.\textsuperscript{10} Under flat band conditions, the quality of measured valence bands and the core level improves considerably, an effect which can be associated with the spatial inhomogeneity in defect distribution on a length scale of the EUV probe (≈ 100 µm). The best experimental results were observed in the case of a broadband CW
light, uniformly illuminating the sample surface, with an intensity of \( \approx 1 \text{ mW/cm}^2 \), which was found to be sufficient to operate under flat band conditions and was always used for all the pump probe traces discussed in the main text.

In contrast to previous reports on hybrid organic-inorganic LHPs, the white light illumination was not found to induce rapid sample degradation, as observed by the appearance of strong secondary reduced Pb core level peaks.\(^{12,13}\) The sample surface was largely intact upon several days of measurements, and the main source of degradation was found to be the illumination by the UV (3.2 eV) femtosecond pump laser. The effect of the UV excitation is to increase the defect concentration over several hours of measurement. For example, the spectrum of Fig. S5 (a), was acquired 20 hrs after in-situ cleavage under UHV conditions and upon continuous irradiation with the fs UV pump laser at a fluence of 25 \( \mu \text{J/cm}^2 \). The estimated density of reduced states is approximately 2% of the surface Pb sites, which increased the band bending from 0.17 eV (measured immediately after cleavage) to 1.1 eV. After this long-term UV illumination, the CW broadband light alone was still sufficient to fully restore flat band conditions. A small in-gap density of states developed upon degradation, decreasing the band contrast. To ensure that radiation damage does not introduce artifacts in the fluence-dependent measurements presented in the main text, the data was collected by varying the fluence in a non-sequential way. Furthermore, after every measurement the single crystal was moved in order to irradiate a fresh area. Reproducibility was tested by repeating the fluence scan on a new cleave of a different sample. The good reproducibility further supports the defect tolerance of charge carriers in CsPbBr\(_3\).\(^{14}\)

The greater resistance to radiation-induced damage of fully inorganic CsPbBr\(_3\) gives us the opportunity to study the material under high excitation densities. The relatively large bandgap of CsPbBr\(_3\) necessitates the use of a UV pump laser. We chose a 3.2 eV photon energy, which makes two-photon photoemission (2PPE) a possible process. The net result of strong 2PPE is to induce additional vacuum space charge effects, which influence the measured time and energy dynamics due to interaction of the escaping probe photoelectrons with
the low kinetic energy pump-induced photoelectron cloud during propagation in vacuum.\textsuperscript{15}

The shift of the 5d\textsubscript{5/2}, as a function of the pump fluence, is illustrated in Fig. S5 (c), for a pump-probe temporal delay of 0 fs (t\textsubscript{0}). After an initial constant value, the band shifts to a higher kinetic energy. The corresponding 2PPE intensity was measured by blocking the probe beam and analysing the photoelectron intensity slightly above the secondary cut-off. After an initial quadratic growth, saturation is observed, at a fluence corresponding to a considerable shift of the 5d\textsubscript{5/2} states. We associate such a saturation with a high density of low kinetic energy photoelectrons.

2.5 Pump-induced vacuum space charge effects

To ensure that our measurements are not prone to artifacts, two aspects have to be taken into consideration. First, the presence of the defect-induced band bending can influence the carrier dynamics via a time-dependent surface dipole; second, the effect of pump-induced vacuum space charge have to be characterized.

The time evolution of the 5d\textsubscript{5/2} kinetic energy as function of pump-probe delay is reported in Fig. S6. In the low fluence regime (Fig. S6 (a)), in the absence of pump-induced space charge, a dynamical shift of a few 10s of meV is measured on a timescale of a few 10s of ps. Since the measurements are performed under flat band conditions due to white light illumination, the dynamics cannot be associated with a transient photovoltage (i.e. a reduction followed by a recovery of the band bending). The reported electron mobility for CsPbBr\textsubscript{3} is generally higher than the hole mobility,\textsuperscript{16–19} and difference in the mobilities of electrons and holes was measured for CsPbBr\textsubscript{3} single crystals grown with the same inverse temperature crystallization method used in this work.\textsuperscript{20} This is similar to the case of GaAs, where an energy shift with the same sign was associated with the photo-Dember effect.\textsuperscript{21} In CsPbBr\textsubscript{3}, the effect is modest compared to GaAs, due to a more balanced \textit{e-h} mobility. As the photo-Dember dynamics develops on a large timescale of 10s of ps, we can therefore safely exclude its significance in the ultrafast surface to bulk carrier transport discussed in
the main text. The inset of Fig. S6 (a) shows a typical transient band shift in the time window comparable to that of the experiment discussed in the main text.

At high fluence, when a considerable pump-induced space charge is present, the qualitative behavior of the energy shift is reversed, increasing before \( t_0 \), followed by a faster decrease at positive time, as shown in Fig. S6 (b). This behaviour is compatible with space-charge induced effects, studied in detail by Oloff et al.,\(^{15}\) and it dominates over the underlying time-dependent surface dipole effects observed at low fluence.

Both processes have a similar qualitative effect on the measured photoelectron kinetic energy in the 0 – 5 ps time window (see inset of Fig. S6 (b)) and induce a reduction of kinetic energy by up to a few 10s of meV for the highest investigated fluences. This uncertainty makes a characterization of the bandgap renormalization more challenging in TR-ARPES data, since it would require a dynamical correction of the kinetic energy. For this reason we concentrate on the measured intensity of the conduction band electrons.

To ensure that the pump space charge does not affect the measured photoelectron intensities, the fitted area of the 5d\(_{5/2}\) level (Fig. S5 (a)) is plotted in Fig. S6 (c) as a function of time delay. The variation is less than 1%, indicating that under our experimental conditions the 2PPE space charge does not affect the measured photoelectron intensities.

### 2.6 Estimation of the photogenerated charge carrier density

In order to properly characterize the dependence of carrier transport properties on electron-hole pair density inside the crystal, the latter has to be carefully estimated considering all of the material optical properties. The average carrier density inside the probed volume was calculated according to the following expression, assuming a two dimensional Gaussian spatial profile \( G(\text{FWHM}_1, \text{FWHM}_2) \) of both the pump and the probe pulses:

\[
N_{\text{probed}} = \frac{P}{f \ast l \ast E_{\text{pump}}} \ast (1 - R) \ast (1 - e^{-a l}) \ast \frac{\int G_{\text{pump}} \ast G_{\text{probe}} \, dS}{\int G_{\text{pump}} \, dS \ast \int G_{\text{probe}} \, dS},
\]

8
where \( G_{\text{pump}} = G(D_{01}/\cos(\theta), D_{02}) \) and \( G_{\text{probe}} = G(D_{11}/\cos(\theta), D_{12}) \), and \( \int dS \) indicates an integral over the sample surface. The corresponding FWHM of the pump and the probe pulses are \( D_{01} = 506 \mu m \), \( D_{02} = 488 \mu m \), and \( D_{11} = 100 \mu m \), \( D_{12} = 140 \mu m \). During the measurements, the angle of incidence \( \theta \) was approximately 30\(^\circ\). \( P \) is the pump power measured with the powermeter; \( f = 6000 \) Hz is the laser’s repetition rate; \( E_{\text{pump}} \approx 5.09 \cdot 10^{-19} J \) is the photon energy of the pump; \( l \approx 5 \text{ Å} \) is the estimated escape depth of photoelectrons; \( \alpha \approx 1.7 \cdot 10^5 \text{ cm}^{-1} \) is the absorption coefficient of the material at 400 nm.\(^{22}\) The sample’s power reflection coefficient can be calculated from Fresnel equation for s-polarized wave:

\[
R = r_s^2 = \left[ \frac{\cos(\theta) - \sqrt{n^2 - \sin^2(\theta)}}{\cos(\theta) + \sqrt{n^2 - \sin^2(\theta)}} \right]^2,
\]

where \( n \) is a complex refractive index of CsPbBr\(_3\) single crystal measured by spectroscopic ellipsometry.\(^{22}\) The estimation was performed under the assumption that one photon generates exactly one electron-hole pair (as discussed in the next subsection). The main uncertainty of the final value comes from the inherent pump power fluctuation.

Within a conventional approach of estimating pump intensity impinging on a surface, the Gaussian-like profile of the pump is approximated with a cylinder of a diameter equal to the FWHM of the Gaussian. The average intensity equal to the height of this cylinder is 1.44 times higher than the actual peak intensity of the pump, leading to an overestimation of the probed carrier density. Following our approach, the carrier density in the near-surface region is calculated by explicitly considering the Gaussian-like profile of the pump and the probe, as shown in Fig. S7, and assuming that the probe pulse practically queries a weighted average of the pump-induced density distribution, resulting in a more realistic value, used in our analysis in the main text.
2.7 Linearity of UV pump absorption

Figure S8 shows the CB electron population at a fixed time delay $t = 150$ fs as a function of the photogenerated electron-hole pair density. The data was acquired in a single measurement to ensure that the pump power was the only variable in the experiment. The excitation density was calculated from pump fluence under an assumption of linear absorption: one UV photon creates exactly one electron-hole pair. The linear fit to the experimental data confirms that the experimental fluence range is well below the onset of two photon absorption process.

2.8 Estimation of the threshold density of polaron overlap

The maximum carrier density at which polaron quasiparticles can still be defined individually can be estimated from simple geometric considerations, as a density at which neighbouring polarons start to overlap:

$$\rho_{pol} = \frac{1}{2 \times (2 \times r_{pol})^3} \approx 4 \times 10^{17} \text{cm}^{-3},$$

where $r_{pol} = 54.85$ Å is the radius of hole polaron, as determined by ARPES.\(^5\) Therefore, as mentioned in the main text, all the experimental carrier densities are way above this threshold, indicating at least a partial breakdown of polaron picture in this regime.

2.9 Independence of $\tau_{fast}$ on the choice of $\tau_{slow}$

The model function used to fit the experimental time traces of CB population consists of the Heaviside step function, multiplied by two exponential decay components with the characteristic times $\tau_{fast}$ and $\tau_{slow}$, all convoluted with a Gaussian to account for the finite temporal resolution of the setup.

Due to the fact that the timescale of $\tau_{slow}$ is comparable to the temporal window of observation, and $\tau_{fast}$ is weakly affected by $\tau_{slow}$ for all the pump fluences (see below) we
decided to perform a global fit of all the experimental traces, where the $\tau_{slow}$ was set as global parameter, while the two exponential amplitudes, a temporal offset and the $\tau_{fast}$ were set as local fit parameters. This resulted in $\tau_{slow} \approx 20\, ps$. The temporal offset was introduced due to the fact that the overlap of pump and probe pulses in time can undergo slow fluctuations of a few 10s of $fs$ between hours-long measurements due to inevitable small thermal drifts in the laboratory throughout the day.

Fixing the $\tau_{slow}$ at 30 ps and 10 ps and re-fitting all the traces individually showed an insignificant influence on the value of $\tau_{fast}$: the typical change was less than 1% and the maximum change was $\sim 4\%$ for the highest pump fluence.

2.10 Pump-induced surface temperature increase

Under an assumption that all of the absorbed energy of a pump pulse transfers impulsively from electronic to lattice degrees of freedom, and the system has sufficient time to dissipate this energy before the arrival of the next pulse (taking into account the 6 kHz repetition rate), we can estimate a theoretical upper limit of the temperature increase inside the crystal as

$$\Delta T = \frac{E_{pump}}{C_{volumetric} \cdot \rho \cdot V},$$

where $E_{pump}$ represents the fraction of the pump pulse energy absorbed within the sample volume $V$. Using the sample heat capacity $C_{volumetric} = 275\, J/kg/K^{23}$ and the volumetric mass density $\rho = 4750\, kg/m^3$, the temperature in the probed volume was found to rise by a maximum of $\sim 30\, K$ for the highest experimental fluence, which is well below the value necessary to achieve a structural phase transition from an orthorhombic to a tetragonal cell symmetry occurring at 361 K.

2.11 Possible additional mechanisms of CB intensity decay

An ultrafast decay of electron population on a $ps$ timescale was previously observed in LHP single crystals by two photon photoemission spectroscopy. In the study of CsPbBr$_3$,\textsuperscript{24} it was attributed to a dynamic decrease of photoionization cross-section of electron upon polaron formation. Notably, the investigation was conducted at a carrier density that is below the
onset of many-body effects in LHPs.\textsuperscript{9,25} In the work on MAPbI\textsubscript{3},\textsuperscript{26} where a carrier density comparable to our lowest value was utilized, a fast component of the CB intensity decay was ascribed to a charge segregation due to a residual surface dipole upon sample cleavage, whereas a slow component was attributed to a diffusive transport of charges out of the detection volume.

Addressing the first hypothesis, the reduction of photoemission probability of electrons due to their localization upon polaron formation is hardly expected at our experimental photocarrier densities, which are well above the threshold of polaron overlap.\textsuperscript{27} As for the built-in fields, they are neutralized by the CW sample illumination, ruling out charge segregation. Furthermore, we exclude the possibility of a significant electric field development via the photo-Dember effect on a ps timescale, as it would require more than an order of magnitude mismatch in the electron and hole mobilities,\textsuperscript{21} whereas the predicted mismatch in CsPbBr\textsubscript{3} is rather small.\textsuperscript{16,17,28}

The trap-assisted non-radiative and the radiative electron-hole recombination manifest themselves in the ns timescale dynamics.\textsuperscript{29} The surface recombination velocity of \(3.7 \cdot 10^3\) cm \(\cdot\) s\(^{-1}\) in CsPbBr\textsubscript{3}\textsuperscript{30} also corresponds to a ns timescale. Furthermore, we rule out a fluence dependence of surface recombination, as all surface states should be saturated already at the lowest experimental carrier density,\textsuperscript{31} which is an order of magnitude higher than the estimated surface trap density in LHP single crystals.\textsuperscript{32}

The influence of the lateral transport out of the probe spot (indicated as (2) in Fig. 1 of the main text) is negligible on the relevant timescales, due to a larger pump spot size (\(\sim 500\) \(\mu m\)), as compared to the probe (\(\sim 100\) \(\mu m\)), as well as their large absolute dimensions, which are at least order of magnitude larger than photocarrier diffusion lengths in LHP single crystals.\textsuperscript{33} The momentum space scattering out of the observation window is forbidden since the accessible CB region has only one single valley, as explained in the main text. We can, therefore, conclude that the fluence-dependent population decay stems from the carrier transport away from the sample surface into the bulk, and is enhanced by AR, which, as a
tri-molecular process, becomes increasingly efficient at high carrier densities.

The reported photo-induced lattice disorder\textsuperscript{34-36} is another mechanism that can modify carrier scattering, and subsequently transport. The lattice disorder can potentially lead to a spatial energetic disorder,\textsuperscript{37} which is considered to be the main limiting factor of the ballistic transport length in low carrier density regime (below $10^{18}$ cm$^{-3}$).\textsuperscript{38}

2.12 Numerical simulation of the electron population decay

The experimentally observed decay of electron population in the near-surface region was simulated by solving the differential Eq. 1 of the main text. It was integrated numerically following the Forward Euler scheme. The values of surface recombination velocity $S$\textsuperscript{30} and mono-molecular bulk recombination coefficient $k_1$\textsuperscript{29} were taken from the corresponding references.

The density dependence $k_3(N)$ was derived from experimental literature data, by employing the heuristic form $k_3 = k_{30}/(1 + N/N_g)^{3/2}$, and adopting the values $k_{30} = 3.6 \cdot 10^{-27}$ cm$^6$ \cdot s$^{-1}$ and $N_g = 7 \cdot 10^{18}$ cm$^{-3}$. The former value was inferred from the carrier lifetime dependence on density for CsPbBr$_3$ in,\textsuperscript{39} assuming that the $k_3$ coefficient used in this reference is an average value within the probed range of densities. The latter value was taken from Ref. 40. This results in a gradual decrease of the tri-molecular bulk recombination coefficient $k_3$ by an order of magnitude from $1.38 \cdot 10^{-27}$ cm$^6$ \cdot s$^{-1}$ to $7 \cdot 10^{-29}$ cm$^6$ \cdot s$^{-1}$ within the range of experimental carrier densities, as shown in Fig. S9.

The solution of the Eq. 1 of the main text yields a spatial and temporal dependence of charge carrier density inside the crystal. Figure S10 shows the evolution of the depth distribution of carrier density plotted every 500 fs for the time delay range from -500 fs to 10 ps. The colorscale of the traces reflects the corresponding time delay: darker colors correspond to earlier time delays, and \textit{vice versa}. Arrival of the pump pulse establishes a nearly exponential profile, which evolves due to various carrier recombination and transport channels, leading to a gradual decrease of the density gradient. A more detailed view of the
carrier density evolution plotted every 25 fs is shown in Fig. S11.

The best agreement between the experimental data in Fig. 4 of the main text and the simulated traces, obtained by solving Eq. 1 of the main text, was achieved using a model for the effective diffusivity based on the literature data, but modified to allow the $D_{\text{eff}}(N)$ to vary at low densities, and assuming a linear dependence in this regime for simplicity, as follows:

$$D_{\text{eff}}(N) = \begin{cases} 
    a \ast N + b & (a \ast N + b) > D_{\text{theor}} \\
    D_{\text{theor}} & (a \ast N + b) \leq D_{\text{theor}}
\end{cases}$$

Figure S12 shows a contour plot depicting the logarithm of the reduced $\chi^2$ of the fit to the experimental data in Fig. 4 of the main text averaged over three traces representing high, intermediate and low carrier density regions, as a function of the $a$ and the $b$ fitting parameters of the model described above. The density-dependent AR coefficient $k_3(N)$ from Fig. S9 was used for the fits. The red crosshair indicates the global minimum, which yields the values of $a = -1.13 \cdot 10^{-18}$ cm$^3$ and $b = 40$ cm$^2$s$^{-1}$, resulting in the smallest discrepancy with the experiment.

For comparison, the simulated traces in Fig. S13 were calculated neglecting the carrier density dependence and using constant values for the diffusivity and the bi- and tri-molecular recombination coefficients. The simulation highlights a tremendous underestimation of the electron population decay at low carrier densities (two bottom traces), as well as a significant overestimation of the population decay at high carrier densities (in the first few picoseconds of the top trace). The values $D \approx 3$ cm$^2$s$^{-1}$, $k_3 \approx 3 \cdot 10^{-28}$ cm$^6$s$^{-1}$ and $k_2 \approx 1.4 \cdot 10^{-10}$ cm$^4$s$^{-1}$ were estimated from the experimental data in Ref. 39 at the highest charge carrier density of $\sim 10^{19}$ cm$^{-3}$. 
Supplementary figures

**Fig. S1.** Fit of the temporal trace reflecting the rise and a decay of the photoemission intensity above the VB maximum of WSe$_2$ caused by prompt band broadening upon photoexcitation. The pump and probe photon energies are 3.2 eV and 24.3 eV, respectively.

**Fig. S2.** Triple-Gaussian fit of the VB EDC of WSe$_2$. The probe photon energy is 24.3 eV.
Fig. S3. Electronic band structure of CsPbBr$_3$ calculated at three levels of theory (indicated in the legend) for high temperature cubic crystal phase.

Fig. S4. Absorption (red) and photoluminescence (blue) spectra of CsPbBr$_3$ single crystals. The inset shows a linear fit to the absorption edge yielding a bandgap value of 2.29 eV.
**Fig. S5.** Saturation of band bending: (a) typical spectrum of Pb 5d core states; (b) positive Pb 5d_{5/2} core level shift upon illumination, indicating downward band bending; (c) shift of the Pb 5d_{5/2} state, as a function of the pump fluence (bottom), and the corresponding 2PPE intensity (top). The spectrum in (a) was obtained using 40 eV probe. The irradiation energy in (b) and (c) was 3.2 eV.

**Fig. S6.** Temporal evolution of (a) the energy shift of Pb 5d states in low fluence regime, (b) the same quantity in high fluence regime, (c) the fitted area of Pb 5d_{5/2} level.
**Fig. S7.** Two dimensional distribution of the photoexcited carrier density in the near-surface region induced by the Gaussian pump pulse (outer orange) overlapped with the Gaussian probe pulse (inner violet), which practically probes a weighted average of this density distribution.

**Fig. S8.** CB electron population measured by TR-ARPES at $t = 150$ fs as a function of calculated excitation density, overlapped with a linear fit to the data.
Fig. S9. Calculated dependence of the Auger recombination coefficient on the carrier density.

\[ k_3 / (1+N/N_g)^{3/2} \]

Fig. S10. Simulated profiles of spatial carrier distribution in the time delay range from -500 fs to 10 ps, plotted with an interval of 500 fs. The trace color reflects a corresponding time delay.
Fig. S11. Complete solution of Eq. 1 of the main text representing carrier density as a function of depth and time delay. A darker color corresponds to a higher carrier density.

Fig. S12. Contour plot of the logarithm of the averaged reduced $\chi^2$ of the fit to three experimental traces from Fig. 4 of the main text representing high, intermediate and low carrier density regions, as a function of $a$ and $b$ fit parameters of the model described in the text. The red crosshair indicates the global minimum.
Fig. S13. Simulated traces (solid lines) for 4 different fluences reflecting charge carrier population decay in the probed volume using constant values of $D \approx 3 \text{ cm}^2\text{s}^{-1}$, $k_3 \approx 3 \cdot 10^{-28} \text{ cm}^6\text{s}^{-1}$ and $k_2 \approx 1.4 \cdot 10^{-10} \text{ cm}^4\text{s}^{-1}$ estimated from the experimental data in Ref. 39 at the highest charge carrier density of $\sim 10^{19} \text{ cm}^{-3}$. The round markers depict the experimental data points. All the traces were normalized and offset to highlight the changes in their shapes regardless of their amplitudes.
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