Extended carrier lifetimes and diffusion in hybrid perovskites revealed by Hall effect and photoconductivity measurements

Y. Chen1,†, H.T. Yi1, X. Wu2, R. Haroldson3, Y.N. Gartstein3, Y.I. Rodionov4, K.S. Tikhonov5, A. Zakhidov3,4, X.-Y. Zhu2 & V. Podzorov1,6

Impressive performance of hybrid perovskite solar cells reported in recent years still awaits a comprehensive understanding of its microscopic origins. In this work, the intrinsic Hall mobility and photocarrier recombination coefficient are directly measured in these materials in steady-state transport studies. The results show that electron-hole recombination and carrier trapping rates in hybrid perovskites are very low. The bimolecular recombination coefficient ($10^{-11}$ to $10^{-10}$ cm$^3$s$^{-1}$) is found to be on par with that in the best direct-band inorganic semiconductors, even though the intrinsic Hall mobility in hybrid perovskites is considerably lower (up to 60 cm$^2$V$^{-1}$s$^{-1}$). Measured here, steady-state carrier lifetimes (of up to 3 ms) and diffusion lengths (as long as 650 μm) are significantly longer than those in high-purity crystalline inorganic semiconductors. We suggest that these experimental findings are consistent with the polaronic nature of charge carriers, resulting from an interaction of charges with methylammonium dipoles.
Hybrid (organic–inorganic) perovskite solar cells represent the recent breakthrough in photovoltaic applications with reported power conversion efficiencies reaching 20% (refs 1–3). In addition to the abundance of the applied studies on this topic, there is a great interest in understanding the fundamental transport and photophysical properties of these materials, the picture of which is not firmly established yet, thereby calling for more reliable experimental studies. For instance, a possibility of high charge-carrier mobility has been considered as one important factor that contributes to the excellent photovoltaic performance of hybrid lead-halide perovskites. Yet, an unambiguous determination of the intrinsic mobility in these materials is missing. Existing experimental values in similar materials range from 0.6 to 50 cm$^2$ V$^{-1}$ s$^{-1}$ (refs 4–6). However, most of the important transport and photophysical parameters, including the carrier mobilities, lifetimes and recombination rates, were so far determined either in materials different from those relevant for high-performance solar cells (for instance, in metallic tin-halide instead of insulated lead-halide perovskites, or perovskites that adopt 2D layered rather than 3D cubic structure) or obtained indirectly, under the conditions less relevant to applications (for instance, in ultrafast spectroscopic experiments, rather than steady-state transport measurements).

Here, we report artefact-corrected Hall effect and steady-state photoconductivity measurements carried out in a range of thin films and single crystals of exemplary hybrid perovskites, CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$, of current interest for photovoltaic applications. Hall effect allows us to directly and independently address the density of photogenerated carriers, $n_{\text{Hall}}$, and the intrinsic carrier mobility, $\mu_{\text{Hall}}$, without assumptions typical for other methods, such as in ultrafast spectroscopic techniques or space-charge-limited current measurements. We find that, in a wide range of illumination intensities, the dynamics of photocarriers is governed by bimolecular electron-hole (e-h) recombination with a very small recombination coefficient $\gamma$ in the range of $10^{-11}$ to $10^{-10}$ cm$^3$ s$^{-1}$, which is comparable to the values observed in the best single-crystalline direct-band inorganic semiconductors, such as GaAs, even though the measured intrinsic Hall mobilities are moderate ($\mu_{\text{Hall}}$ of up to 60 cm$^2$ V$^{-1}$ s$^{-1}$ in perovskite single crystals) and smaller than $\mu$ in typical inorganic semiconductors by 1–3 orders of magnitude. In addition, the carrier lifetime, $\tau$, and diffusion length, $l$, directly measured in our steady-state transport experiments are found to be remarkably long ($\tau$ is up to 30 $\mu$s and $l$ is up to 23 $\mu$m in polycrystalline films, and up to 3 ms and 650 $\mu$m in single crystals, respectively). Our experiment thus provides a direct steady-state measurement quantitatively revealing a low-rate photocarrier recombination and negligible trapping, as well as extremely long carrier lifetimes and diffusion lengths in hybrid perovskites. While in agreement with some of the recent theoretical predictions$^7$–$^{10}$, these results accentuate important questions as of the physical origins of the found intrinsic carrier mobility, e-h recombination and trapping rates in these materials synthesized via inexpensive vapour- or solution-based routes at temperatures close to room temperature. We propose rationalization of some of our findings based on the picture of re-organization of the methylammonium dipoles around the charge carriers. This interaction leads to carrier relaxation into polarons, whose properties differ from the bare band carriers$^{11–15}$.

**Results**

**a.c. Hall effect measurements of charge-carrier mobility.** It should be emphasized that unambiguous determination of the intrinsic (that is, not dominated by traps) charge-carrier mobility requires precise Hall effect measurements, which are quite challenging in highly resistive materials with relatively low $\mu$, such as organic semiconductors or the hybrid perovskites studied here (see, for example, ref. 14). The major challenges are associated with a very high resistivity of pure stoichiometric perovskites (greater than $10^5$), related to the negligible (in the dark) density of charge carriers, and a poor signal-to-noise ratio in conventional d.c. Hall measurements of low-$\mu$ materials. To overcome these difficulties, here, we have developed a specialized highly sensitive a.c. Hall measurement technique, corrected for the Faraday-induction artefacts, in which a low-frequency a.c. magnetic field, $B$, is applied perpendicular to the sample’s surface, while a d.c. current, $I$, is passed through the sample, and an a.c. Hall voltage, $V_{\text{Hall}}$, is detected across the channel by a phase-sensitive lock-in technique, which allows to markedly increase the signal-to-noise ratio$^{12}$. A parasitic Faraday-induction electro-motive force, occurring in a.c. Hall measurements at the same frequency as $V_{\text{Hall}}$, is usually comparable to the actual Hall voltage signal and can easily compromise these measurements. Therefore, Faraday-induction-corrected a.c. Hall measurements, as implemented here in perovskites, are absolutely necessary to obtain reliable data (see the ‘Methods’ section, Supplementary Fig. 1 and Supplementary Note 1$^5$). Pure CH$_3$NH$_3$PbI$_3$ samples are highly resistive in the dark (typical $R \gtrsim 100$ G$\Omega$), and thus we utilize a steady-state monochromatic photo-excitation ($\lambda = 465$ nm) to generate a population of carriers and be able to measure Hall effect. In CH$_3$NH$_3$PbBr$_3$ single crystals, we were able to measure a Hall effect in the dark as well, because these crystals are weakly conducting in the dark (at a level of 50 M$\Omega$). We perform all our measurements in a 4-probe/Hall bar geometry to account for contact-resistance effects and ensure that channel conductivity, $\sigma$, as well as the Hall mobility and carrier density, $\mu_{\text{Hall}}$ and $n_{\text{Hall}}$, are determined correctly.

**Steady-state photoconductivity vs. light intensity.** Three types of hybrid perovskite samples were used in our study (Fig. 1). (a) Semi amorphous, solution-grown thin films, (b) polycrystalline, vapour-grown thin films and (c) highly ordered, solution-grown single crystals. The microscopy and X-ray diffraction clearly show that the vapour-processed films have a much better crystallinity than the solution-processed ones, and our single crystals have excellent quality (see Fig. 1 and see the ‘Methods’ section for details).

We have found that all our high-quality (stoichiometric) samples exhibit a very low dark conductivity. Nevertheless, a significant photoconductivity is observed in all of them. Figure 2 shows typical dependences of a steady-state photoconductivity, $\sigma_{\text{PC}}$, on photo-excitation density, $G$, which always follows a power law, $\sigma_{\text{PC}} \propto G^2$, with the exponent $\alpha = 1$ or $1/2$ (linear or square-root regimes). Photo-excitation density, $G$, is defined as the incident photon flux $F$ (in cm$^{-2}$ s$^{-1}$) divided by the absorption length of the material.

The observed $\sigma_{\text{PC}}(G)$ dependence can be understood in terms of charge-carrier monomolecular decay (trapping in the linear regime) or bimolecular decay (e-h recombination in the square-root regime). The photocarrier density, $n$ ($n \equiv n_e \equiv n_h$), in steady-state measurements is found from the following rate equation, with $\mathrm{d}n/\mathrm{d}t = 0$ at dynamic equilibrium (see, for example$^{16}$):

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \kappa G - \frac{n}{\tau_{\text{tr}}} - \gamma n^2 = 0.$$  

Here, $\kappa G$ is the rate of carrier generation via photon absorption resulting in production of free electrons and holes with...
probability $\kappa$ per photon (the photocarrier-generation efficiency). The second and third terms represent the two channels of carrier decay: the trapping and e-h recombination, where $\tau_{tr}$ is the trap-limited carrier lifetime (an average time carriers diffuse before being trapped), and $\gamma$ is the coefficient of e-h recombination. In the carrier density range probed here, we do not see any experimental evidence of the third-order (Auger) processes, which are therefore excluded from equation (1). At low photo-excitation intensities, when the concentration of electrons and holes is small, the dominant process limiting the carrier lifetime is trapping, and $\gamma n^2$ term in equation (1) can be neglected, leading to a linear regime in photoconductivity: $\sigma_{PC} = \epsilon m T = \epsilon m \tau_{tr} G$, where $e$ is the elementary charge. With increasing excitation intensity, the bimolecular recombination eventually becomes dominant, resulting in a transition from the linear to a sublinear regime: $\sigma_{PC} = \epsilon m (k/\gamma)^{1/2} G^{1/2}$, obtained from equation (1) by neglecting the $n/\tau_{tr}$ term. Figure 2 shows that these two regimes are indeed what is observed in hybrid perovskites. Highly crystalline samples exhibit bimolecular recombination regime ($x = 1/2$) in a wider range of excitation intensities, which is consistent with the higher $\sigma_{PC}$ and $\mu_{Hall}$ in the crystal samples (see below).

Figure 2 | Steady-state photoconductivity measured as a function of photo-excitation density in thin films and single crystals of hybrid perovskites. Measurements are carried out by 4-probe technique under a cw photo-excitation with a blue light ($\lambda = 465\text{ nm}$) in CH$_3$NH$_3$PbBr$_3$ single crystals (red squares), vapour-grown polycrystalline CH$_3$NH$_3$PbI$_3$ films (green triangles) and solution-grown semi amorphous CH$_3$NH$_3$PbI$_3$ films (black circles). Dashed lines are the power law fits, $\sigma_{PC} \propto G^x$, with the exponents $x = 1$ or $1/2$ (as indicated). It is clear that bimolecular e-h recombination ($x = 1/2$) dominates the behaviour at high photo-excitation densities (note the double-log scale).

Hall measurements under photo-excitation and in the dark. To decouple the carrier density and mobility in $\sigma_{PC} = \epsilon n \mu$ and obtain the microscopic parameters describing the carrier dynamics, $\tau_{tr}$ and $\gamma$, from the rate equation for $n$ (equation (1)) and experimental data, one needs to know the intrinsic charge-carrier mobility $\mu$. For this purpose, we have performed Hall effect measurements, as discussed above, using 4-probe/Hall-bar device structures (Fig. 3a) and a variant of an a.c. Hall measurement technique (Fig. 3b) specifically adjusted for these materials (see the ‘Methods’ section, Supplementary Fig. 1 and Supplementary Note 1). A typical measurement result is shown in Fig. 3c: a very clear and quiet a.c. Hall signal as detected in a solution-grown CH$_3$NH$_3$PbI$_3$ thin film that has a Hall mobility of only $\mu_{Hall} = 1.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Reliable Hall measurements with such
an excellent signal-to-noise ratio in highly resistive systems with carrier mobilities as low as 1 cm² V⁻¹ s⁻¹ are unprecedented. For comparison, conventional d.c. Hall measurements performed in a perovskite single crystal with a much higher mobility, \( \mu_{\text{Hall}} = 11 \text{ cm}² \text{ V}⁻¹ \text{ s}⁻¹ \), shown in Fig. 3d, evidently exhibit a much noisier signal. It is clear that Faraday-induction-corrected a.c. Hall measurements are far superior to the conventional d.c. technique in terms of the signal-to-noise ratio, even though it uses a smaller magnetic field (r.m.s. 0.23 T).

As expected for pure undoped band insulators, our CH₃NH₃PbI₃ samples are highly resistive in the dark (with a typical sample resistance >100 GΩ). Thus, we used a cw photo-excitation to generate photocarriers and perform steady-state photo a.c. Hall measurements. In a system with photogenerated electrons and holes \( n_e \approx n_h \equiv n \) and a negligible concentration of dark carriers, Hall voltage is given by:

\[
V_{\text{Hall}} = \frac{W}{L} \cdot B \cdot V_L \cdot (\mu_h - \mu_e),
\]

where \( W \) and \( L \) are the channel’s width and length, respectively, \( V_L \) is the longitudinal voltage drop along the channel (corrected for contact effects by using the 4-probe technique), and \( \mu_h, \mu_e \) are the mobilities of holes and electrons, respectively. Equation (2) shows that photo Hall effect measurements yield the difference between the electron and hole mobilities, rather than their absolute values. In the context of the perovskites under study, recent calculations showed that \( \mu_e \) and \( \mu_h \) in these materials should differ from each other by an amount comparable to the mobilities themselves. Indeed, theoretical calculations have consistently indicated that while effective masses of electrons, \( m_e \), and holes, \( m_h \), have the same order of magnitude, there is also a noticeable difference between the two, ranging from 20 to 200%, depending on the specific computational method used. A recent THz spectroscopy study also suggests a difference of a factor of 2 between the electron and hole mobilities.

Therefore, even though precise values of \( \mu_e \) and \( \mu_h \) cannot be obtained from photo Hall measurements, the difference, \( \Delta \mu \equiv \mu_h - \mu_e \), extracted from equation (2) would yield a faithful representation. In turn, the carrier density obtained from the photo Hall effect measurements is: \( n = n_e + n_h = \sigma_{\text{PC}}/(e \cdot \mu) \), which is also a good approximation for the actual density of photogenerated charges. The data presented below are analysed using this association. The dark Hall effect measurements possible in weakly conducting single-crystal CH₃NH₃PbBr₃ samples give further credence to the approach.

Figure 4 presents Hall effect data for a variety of hybrid perovskite samples. Fig. 4a shows that Hall mobility, \( \mu_{\text{Hall}} = 8 \pm 0.4 \text{ cm}² \text{ V}⁻¹ \text{ s}⁻¹ \), measured in a polycrystalline CH₃NH₃PbI₃ film remains almost constant over the range of nearly three orders of magnitude in light intensity (the error is defined by the fluctuations in Fig. 4a). The 4-probe photoconductivity, \( \sigma_{\text{PC}} \), and the density of photogenerated charge carriers, \( n_{\text{Hall}} \), determined from the simultaneous longitudinal
σPC and Hall effect measurements in these polycrystalline films are plotted in Fig. 4b. Within the entire measurement range, the carrier density dependence on the illumination intensity exhibits $\alpha \approx 1$, power law: $n_{\text{Hall}} \propto G^{1/2}$. We emphasize that independent measurements of $\mu_{\text{Hall}}$ as a function of photo-excitation density are essential for obtaining $n_{\text{Hall}}(G)$ dependence and therefore for determination of the microscopic transport parameters, $\tau_p$ and $\gamma$, by using equation (1) to fit the data. With the density of photogenerated carriers determined experimentally, we can now interpret their dynamics with the help of equation (1). As pointed out above, under a steady-state photo-excitation, equation (1) gives $n \approx (h/\omega)^{1/2} \cdot G^{1/2}$ in the regime governed by a bimolecular recombination, that is, when the carrier trapping time $\tau_r$ well exceeds the time of e-h recombination $\tau_{tr}$, $\tau_{tr} \gg \tau_r \equiv (\gamma n)^{-1}$. Fitting the experimental Hall carrier density in Fig. 4b with this $n(G)$ relationship yields the upper bound for the bimolecular e-h recombination coefficient $\gamma$ in polycrystalline perovskite films, $\gamma \lesssim 3 \times 10^{-11}$ cm$^3$ s$^{-1}$ (for the photocarrier-generation efficiency $k \leq 100\%$).

The measurements shown in Fig. 4 can also be used to directly estimate the steady-state charge-carrier lifetime, either $\tau_{tr}$ or $\tau_r$, and diffusion length, $l$. Indeed, since bimolecular recombination ($\alpha = 1/2$) apparently dominates in the entire range of photon densities in Fig. 4b, we must have the condition $n_{\text{Hall}} \ll h \gamma n^2$ (or, $\tau_{tr} \gg \tau_r \equiv (\gamma n)^{-1}$) fulfilled for all the incident photon intensities, including the lowest one, at which $n_{\text{Hall}} = 9 \times 10^{14}$ cm$^{-3}$ (Fig. 4b). Therefore, the effective trap-limited carrier lifetime $\tau_{tr}$ in the disordered polycrystalline film in Fig. 4b must be longer than the lifetime limited by bimolecular e-h recombination, $\tau_{tr} > \tau_r \approx 30 \mu$s. This estimate shows that even in disordered CH$_3$NH$_3$PbI$_3$ thin films, charge carriers have an extremely long lifetime, as far as trapping is concerned, and thus the effective density of the corresponding deep traps must be very low, or the traps must be electronically passivated. The corresponding lower bound of trap-limited carrier diffusion lengths in these polycrystalline perovskite films is: $l = (D \tau_{tr})^{1/2} \approx 23 \mu$m. Here, we needed the Hall mobility again to calculate the diffusion coefficient, $D \sim \mu_{\text{Hall}}^2 k_B T/e$, where $k_B$ is the Boltzmann constant and $T = 300$ K. Note that negligible trapping and a very long diffusion length, greater than the grain size in our polycrystalline films (Fig. 1b), are consistent with the recent theoretical studies predicting the presence of only shallow traps and benign grain boundaries that do not trap carriers in perovskites$^{9,10}$. Of course, given the dominant e-h recombination, the actual carrier lifetime in the $\alpha = 1/2$ regime is a decreasing function of photo-excitation density $G$: $\tau_r = (\gamma n)^{-1}$ (see also$^{16}$).

Figure 4c shows $n_{\text{Hall}}$ and $\mu_{\text{Hall}}$ in six different solution and vapour-grown polycrystalline thin films. In general, vapour-grown samples have an appreciably higher $\mu_{\text{Hall}}$ consistent with their better crystallinity. In sharp contrast, $n_{\text{Hall}}(G)$ does not seem to correlate much with the preparation method and mobility. Indeed, while $\mu_{\text{Hall}}$ differs among the six samples by as much as a factor of 20, $n_{\text{Hall}}$ varies only within a factor of two. Correspondingly, $\gamma$ values are also very similar for all these samples, $\gamma \sim (1-5) \times 10^{-11}$ cm$^3$ s$^{-1}$. This suggests that while film morphology has a clear effect on charge transport, it has little effect on photocarrier generation and recombination. This is consistent with the notion that bimolecular recombination in this system is not governed by carrier diffusion, therefore we do not see a strong correlation between the recombination dynamics and charge-carrier mobility.

Finally, we have performed Hall measurements in CH$_3$NH$_3$PbBr$_3$ single crystals (Fig. 4d). One important difference in this case is that these crystals are weakly conducting in the dark, which allows us to perform Hall effect measurements in the dark and obtain the mobility of holes ($\mu_{\text{Hall}} \approx 60 \pm 5$ cm$^2$ V$^{-1}$ s$^{-1}$),...
without having an ambiguity of charge compensation as in photo Hall measurements. Photoconductivity in these crystals is much higher than that in thin films and also exhibits a well-defined \( \alpha = \frac{1}{2} \) behaviour (Fig. 4d). A similar analysis of \( n_{\text{Hall}}(G) \) dependence shows that the e-h recombination coefficient in these crystals is \( \gamma \approx 8 \times 10^{-11} \text{ cm}^2 \text{s}^{-1} \) (for more details on the extraction procedure see Supplementary Note 2). By defining the effective recombination-limited carrier lifetime again the extraction procedure see Supplementary Note 2). By strongly suppressing in these materials. We must add that bimolecular recombination, thus indicating again that trapping is \( \text{equation 3) then yields the recombination coefficient:} \)

\[
\gamma \approx 1.4 \times 10^{-10} \cdot \frac{e(E_g - E_{\text{opt}})/k_B T}{\text{cm}^3 \text{s}^{-1}}.
\]

Here, the prefactor was calculated with \( T = 300 \text{ K} \) and \( m_e \approx m_0 = m = 0.2m_0 \) (\( m_0 \) being the free electron mass). Equation (6) features the absorption onset parameter denoted \( E_{\text{opt}} \), which is equal to 1.553 eV in the parameterization of ref. 28. The excitonic (e-h attraction) effects are known to reduce the onset of optical absorption in comparison with the semiconductor band-gap in perovskites (see, for example, the discussion of excitons in ref. 29). One can approximately assess the resulting exponential factor in equation (6) from the corresponding exciton binding energy \( E_h \). For \( m = 0.2m_0 \) and the relative permittivity equal to 5, for instance, \( E_h \approx 54 \text{ meV} \), indicating that the exponential factor is of the order of 10, which would make result (6) for \( \gamma \) larger than our experimental values by about one order of magnitude. The discrepancy here might result from the underestimate of \( n_{\text{eq}} \) by equation (5) for the conventional band carriers, and the larger values of \( n_{\text{eq}} \) would lead to a better agreement with the experiment. We suggest that large concentrations \( n_{\text{eq}} \) might be actually realized in perovskites due to the interaction of band charge carriers with methylammonium dipoles, as illustrated in Fig. 5.

**Theoretical estimates of e-h recombination coefficients.** E-h recombination in semiconductors is a fundamentally important process, and various approaches have been developed for assessing the corresponding kinetic coefficient \( \gamma \). In one approach, for instance, \( \gamma \) is associated with the product \( sv \) of the Coulomb capture section \( s \) and carrier thermal velocity \( v \) (ref. 16). In the case of disordered organic and inorganic semiconductors, recombination of charge carriers is often described by the Langevin model, which leads to \( \gamma = \frac{\alpha_0 \sigma_0}{q_0^2} \) for the recombination coefficient, where \( \alpha_0 \) and \( \sigma_0 \) are the dielectric permittivities of vacuum and the material, respectively. Evaluating these expressions for our systems would yield estimates of \( \gamma \) on the order of \( 10^{-6} \text{ cm}^2 \text{s}^{-1} \) or higher, that is 4–5 orders of magnitude greater than what we find experimentally. One, of course, realizes that the above models, evidently not applicable to our case, refer to the e-h collision events rather than to the radiative recombination per se. A more appropriate approach that was successfully applied to the actual radiative recombination in inorganic semiconductors is based on the van Roosbroek–Shockley’s theory rooted in the principle of detailed balance (for reviews, see, for instance, refs 24,25). This theory, in particular, explains well the values of \( \gamma \approx 10^{-10} \text{ cm}^2 \text{s}^{-1} \) exhibited by high-purity direct-band inorganic semiconductors, such as, for instance, GaAs (see also http://www.ioffe.ru/SVA/NSM/Semicond/index.html), which, remarkably, are comparable to the values we extract from our observations in hybrid perovskites. In the van Roosbroek–Shockley’s approach, the radiative recombination coefficient \( \gamma \) is established by the system’s properties in the thermal equilibrium (that is, in the dark):

\[
\gamma = \frac{R_{\text{eq}}}{n_{\text{eq}}^2}, \quad (3)
\]

where, \( R_{\text{eq}} \) and \( n_{\text{eq}} \) are the equilibrium (dark) recombination rate and concentration of electrons (equal to that of holes), respectively. Furthermore, \( R_{\text{eq}} \) is related thermodynamically to the optical properties of the system as follows:

\[
R_{\text{eq}} = \frac{2}{\pi^2 c^3} \int_0^{\infty} n_e^2 k_0 \exp \left( \frac{E_0}{k_B T} \right) \text{d} \omega - \frac{1}{T}. \quad (4)
\]

utilizing the frequency \( \omega \)-dependent refraction, \( n_e(\omega) \), and extinction, \( \kappa(\omega) \), coefficients. An assessment of equation (3) can be made using model considerations (as illustrated in Supplementary Note 3). Even more attractively, one can use the actual experimental optical data to evaluate \( R_{\text{eq}} \) in equation (4), for which here we use the optical parameters (see Supplementary Fig. 2 and Supplementary Note 3) of CH3NH3PbI3 perovskite extracted from accurate ellipsometric measurements in ref. 28. On the other hand, the dark carrier concentration at the thermal equilibrium \( n_{\text{eq}} \) is not measured directly. If one were to use the standard textbook expression for a non-degenerate semiconductor with energy gap \( E_g \) separating two parabolic bands25:

\[
n_{\text{eq}}^2 = \frac{(m_e m_h k_B T)^3}{2\pi^3 \hbar^6} e^{-\frac{E_g}{k_B T}}, \quad (5)
\]

accounting for polaronic effects. Theoretical calculations by Frost et al. demonstrate that the methylammonium dipoles in hybrid perovskites carry a significant dipole moment, \( P = 2.29 \text{ D} \),
and create a rough potential landscape at the nanoscale, but can be easily rotated or locally aligned by overcoming a small rotational energy barrier, $U_{\text{rot}} \approx 1 \text{kJ mol}^{-1}$ (1.6 $\times 10^{-21}$ J or 10 meV per dipole). Here, we propose that a charge carrier moving through the perovskite lattice may itself induce a local orientational rearrangement of the surrounding methylammonium dipoles tending to align them along its electric field (Fig. 5), thus resulting in a type of a dipolar polaron, conceptually similar to polarons known in ionic crystals and polar semiconductors. The estimates outlined in Supplementary Note 3 show that such polarons in perovskites should be characterized as intermediate-coupling polarons, with the dimensionless electron–phonon coupling constant $\zeta_{e-p} \approx 2.5$ being a good representative value for the interaction of the band carriers with the longitudinal dipolar vibrational modes of energy $h\omega_{\text{ph}} \approx 10$ meV. The ‘dressing’ of a band carrier by a phonon cloud is known to change its properties: the standard band carrier dispersion $E(k) = \hbar^2 k^2/2m$ would be modified to the polaronic energy-momentum relation $E_{\text{p}}(k)$. Two aspects of this modification are important here.

First, polaron formation is energetically favorable, resulting in the polaronic energy shift $E_{\text{p}}(0) \approx \zeta_{e-p} h\omega_{\text{ph}}$. The effective band-gap for the equilibrium concentration of electron- and hole-polarons is thus reduced: $E_{\text{g}} \rightarrow E_{\text{g}}^\text{p}(0) + E_{\text{g}}^\text{b}(0)$. With the estimates above, this reduction largely negates the effect of the exciton binding $E_{\text{p}}$ and substantially decreases the exponential factor in equation (6). (One could also say that the thermal dissociation of an exciton into a polaron pair is more efficient than into a pair of band carriers.) Second, polarons are ‘heavier’ than the band carriers. While the renormalized mass

$$m_{\text{p}}(0) = \frac{m}{1 + \zeta_{e-p}/6},$$

the actual changes are even more significant, as the polaron dispersion becomes non-parabolic (see Fig. 6 with the accompanying caption, Supplementary Figs 3,4 and Supplementary Note 3). This results in the increased density of the polaronic states and corresponding increase in the carrier diffusion coefficient $D_{\text{p}}$.

**Figure 6 | Polaron energy-momentum relation.** This plot compares the shape of the energy-momentum curves for different models calculated with the electron–phonon coupling constant $\zeta_{e-p} \approx 2.5$. The energy is measured in units of the vibrational energy $h\omega_{\text{ph}}$ and the wave number in units of $k_p = (2m\omega_{\text{ph}}/\hbar)^{1/2}$. The dashed lines show the parabolic dispersion, for the bare band carrier (black) and for the polaronic carrier with renormalized mass $m_{\text{p}}$. The solid lines display the non-parabolic dispersion obtained with variational calculations, according to Lee-Low-Pines theory (green curve) and according to Larsen theory (red curve). The latter is shown in the limited range of its applicability, but it is this type of the dispersion that was actually confirmed in the state-of-the-art diagrammatic Monte-Carlo calculations.

**Discussion**

While currently there is no analytical framework that would afford quantitatively reliable calculations of the interplay of excitonic and polaronic effects in the relevant parameter range (all energy parameters: $k_BT$, $h\omega_{\text{ph}}$, polaronic and excitonic bindings, are of the same order of magnitude), the above estimates and analysis demonstrate that the polaronic effects might provide an explanation that brings the experimental optical data and our measurements of the radiative recombination coefficient $\gamma$ in a reasonably good agreement with each other. Indeed, the experimental estimates for $\gamma$ derived above from the Hall effect measurements span the range of $10^{-11}$ cm$^2$ s$^{-1}$. On the other hand, the polaronic effects we discussed evidently lead to a substantial decrease of the value in equation (6) evaluated without such effects and likely reducing this estimate below $10^{-10}$ cm$^2$ s$^{-1}$. Given the fact that photo Hall measurements could precisely address only the difference of the hole and electron mobilities, and some uncertainty in theoretical estimates, the consistency of our results appears quite satisfactory. In addition, we note that the non-parabolic polaronic dispersion displayed in Fig. 6 clearly features carrier group velocities $v_{\gamma} = \partial E_{\gamma}(k)/\hbar k$ considerably lower than those, $hk/m$, of the bare band carriers. This, of course, leads to lower carrier mobilities as indeed observed in our experiments.

Another important experimental observation is that we have not found the monomolecular decay regime (trapping) down to rather low carrier densities, $n \approx 10^{12}$ cm$^{-3}$ in thin films, and $5 \times 10^{12}$ cm$^{-3}$ in single crystals (Fig. 4). If present, such a regime would manifest itself as a linear $\sigma_{\gamma}(G)$ dependence ($\gamma = 1$). The absence of trapping is exactly the reason why bimolecular e-h recombination dominates down to a much lower carrier density, leading to a remarkably long carrier lifetime and diffusion length at diluted photo-excitation densities, consistent with prior observations. In direct-band inorganic semiconductors, even though similarly small values of $\gamma = 10^{-11} - 10^{-10}$ cm$^2$ s$^{-1}$ are observed in high-purity crystalline samples, achieving a millisecond carrier lifetime and nearly a millimetre-long diffusion length is unheard of. Ordinarily, other recombination mechanisms such as trapping on recombination centres (or even Auger processes) would start to dominate at a higher crossover carrier density, given the rather small e-h recombination probability. In fact, in well-optimized high-purity single crystals of GaAs, InP or InAs, $\tau$ and $l$ are a few $\mu$s and a few tens of $\mu$m at best, indicating that photo Hall measurements could precisely address only the difference of the hole and electron mobilities, and some uncertainty in theoretical estimates, the consistency of our results appears quite satisfactory. In addition, we note that the non-parabolic polaronic dispersion displayed in Fig. 6 clearly features carrier group velocities $v_{\gamma} = \partial E_{\gamma}(k)/\hbar k$ considerably lower than those, $hk/m$, of the bare band carriers. This, of course, leads to lower carrier mobilities as indeed observed in our experiments.

**Figure 6 | Polaron energy-momentum relation.** This plot compares the shape of the energy-momentum curves for different models calculated with the electron–phonon coupling constant $\zeta_{e-p} \approx 2.5$. The energy is measured in units of the vibrational energy $h\omega_{\text{ph}}$ and the wave number in units of $k_p = (2m\omega_{\text{ph}}/\hbar)^{1/2}$. The dashed lines show the parabolic dispersion, for the bare band carrier (black) and for the polaronic carrier with renormalized mass $m_{\text{p}}$. The solid lines display the non-parabolic dispersion obtained with variational calculations, according to Lee-Low-Pines theory (green curve) and according to Larsen theory (red curve). The latter is shown in the limited range of its applicability, but it is this type of the dispersion that was actually confirmed in the state-of-the-art diagrammatic Monte-Carlo calculations.

$E_{\text{p}}^\text{b}(0)$ and $E_{\text{p}}^\text{b}(0)$ are even more significant, as the polaron dispersion becomes non-parabolic (see Fig. 6 with the accompanying caption, Supplementary Figs 3,4 and Supplementary Note 3). This results in the increased density of the polaronic states and corresponding increase in the carrier diffusion coefficient.

$D_{\text{p}}$.
than the energy gained associated with a dipole-trap interaction, for instance, if estimated as: \( P \cdot (\frac{1}{2} \cdot \frac{d\sigma}{d\theta}) \sim 10^{-7} \) to 75 eV (for \( P = 2.29 \) D). The re-arranged dipoles would thus reduce the defect’s trapping cross section. Such a defect decoration would be reminiscent of the recently observed trap healing effect at two-dimensional semiconductor/polymer interfaces, with the important distinction that in hybrid perovskites the functional (rotationally responsive) dipoles are naturally available throughout the entire bulk of the sample. The question arises if the dipole rearrangement effect could be greater than that throughout the entire bulk of the sample. The question arises if important distinction that in hybrid perovskites the functional properties of these materials are quite different from those of conventional organic or inorganic semiconductors. We emphasize that our study determines these important transport parameters directly, from steady-state transport measurements, relevant to practical applications. The dipolar polaron model has been found helpful to explain the observed relatively low intrinsic carrier mobilities and radiative recombination rates.

Methods

Growth of hybrid perovskite thin films and single crystals. For fabrication of thin-film perovskite samples, we followed the published procedures. Polycrystalline films and single crystals, respectively and diffusion lengths (up to 23 and 650 \( \mu m \) in films and crystals, respectively). These measurements provide a direct and conclusive evidence of low e–h recombination rates and remarkably weak charge trapping in hybrid perovskites. They show that photophysical properties of these materials are quite different from those of conventional organic or inorganic semiconductors. We emphasize that our study determines these important transport parameters directly, from steady-state transport measurements, relevant to practical applications. The dipolar polaron model has been found helpful to explain the observed relatively low intrinsic carrier mobilities and radiative recombination rates.

Device fabrication. Devices in Hall bar geometry were fabricated by depositing Au or Ti through a shadow mask on freshly grown films or crystals. After wiring, the device was capped under vacuum \( (10^{-3} \) Torr) with a protective PPFE (perfluoropolyether) oil, which is a chemically and electrically inert perfluorinated polymer. We find that PPFE can effectively protect samples from degradation due to moisture and other environmental factors. Control tests showed that PPFE does not cause any qualitative changes in the electrical properties of hybrid perovskite samples.

Magneto-transport and photoconductivity measurements. All measurements in this work were carried out at room temperature. a.c. Hall measurements were performed in an a.c. magnetic field of \( B = 0.23 \) T (r.m.s.), referenced to a Stanford Research lock-in amplifier that measures a.c. \( V_{Hall} \). To reduce the parasitic Faraday induction, frequencies below 1 Hz were typically used. More importantly, \( V_{Hall} \) generated across the sample at a non-zero d.c. excitation (\( I \neq 0 \)) was always compared with that generated at zero current (\( I = 0 \)), which yields a pure, Faraday-induction-corrected, Hall voltage.\(^1\) We have verified that \( V_{Hall} \) in all our samples was independent of the frequency in the range 0.3 to 5 Hz, which confirms that undesirable Faraday-induction signal was eliminated. Keithley 6221 current source was used to drive a d.c. excitation current through the sample. Calibration of our a.c. Hall setup has been done by carrying out measurements of a control Si sample with known carrier density and mobility. Longitudinal (photo)conductivity was measured by 4-probe technique, which ensured that ambiguities associated with sample resistance were eliminated. It is important to emphasize that although 2-probe \( \rho_{Hall} \) also exhibits a sublinear power dependence (\( \rho_{Hall} \propto C^2 \)), with \( C < 1 \), the power exponent \( z \) in 2-probe measurements may vary in a wider range from sample to sample due to contact effects. In contrast, 4-probe photoconductivity systematically shows \( z = \frac{1}{2} \) at high illumination intensities, which signifies a regime governed by bimolecular recombination.

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Author contributions

V.P. designed the research project and supervised the experiment. Y.C. and H.T.Y. performed device fabrication and measurements. Y.C., X.W., R.H., X.-Y.Z and A.Z. grew perovskite thin films and single crystals, Y.N.G., Y.I.R. and K.S.T. performed theoretical calculations, Y.C., Y.N.G. and V.P. wrote the paper. All authors discussed the results.

Additional information

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