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Title: Long-Range Balanced Electron and Hole Transport Lengths in Organic-Inorganic CH₃NH₃PbI₃

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Abstract: Low temperature solution processed photovoltaics suffer from low efficiencies due to poor exciton/electron-hole diffusion lengths (typically about 10 nanometers). Recent reports of highly efficient CH₃NH₃PbI₃-based solar cells in a broad range of configurations raise a compelling case for understanding the fundamental photophysical mechanisms in these materials. By applying femtosecond transient optical spectroscopy to bilayers that interface this perovskite with either selective electron or selective hole extraction materials, we have uncovered concrete evidence of balanced long-range electron-hole diffusion lengths of at least 100 nm in solution processed CH₃NH₃PbI₃. The high photoconversion efficiencies of these systems stem from the comparable optical absorption length and charge carrier diffusion lengths, transcending the traditional constraints of solution processed semiconductors.

One Sentence Summary: Long-range balanced carrier diffusion lengths are observed in CH₃NH₃PbI₃ overcoming the fundamental carrier diffusion bottleneck that limits solution processed photovoltaics.

Main Text: An ideal solar cell material should combine good optical absorption characteristics with efficient charge transport properties. Low temperature solution processed

light harvesting films prepared by techniques such as spin coating and chemical bath deposition are typically amorphous or poorly crystalline (1-3), consequently suffering from poor charge carrier transport (4). This limitation necessitates device designs that decouple light absorption and charge carrier transport lengths, including light trapping strategies such as plasmonics (5, 6) as well as the sensitized solar cell architecture (7, 8). The recent development of organic-inorganic halide perovskite materials such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ as light harvesters in solid state sensitized solar cells has led to reports of impressive efficiency values of up to 15% (9). This remarkable material has been employed in a variety of photovoltaic architectures. A configuration employed by Kim et al. (10) and Heo et al. (11), sandwiches the thin perovskite layer between a rough mesoporous TiO_2 photoanode and a hole transporting layer such as (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobi-fluorene (Spiro-OMeTAD). Lee et al. (12) have shown that efficient solar cells can be fabricated by replacing the TiO_2 photoanode with an insulating Al_2O_3 scaffold – implying good electron transport properties. Surprisingly, Etgar et al. (13) reported an efficiency of 5.5% in a configuration without the hole transporting layer – indicating good hole transport properties. These indications of ambipolar charge transport capabilities are supported by a recent report by Ball et al. (14) which demonstrated that ~350 nm thick planar films sandwiched between a TiO_2 compact layer and a hole transporting layer can generate short circuit current densities of 15 mA/cm^2 . These reports together imply that the electron and hole transport lengths within these organic-inorganic hybrid materials are high. Nonetheless, the innate dynamics of the photoexcited electrons and holes in $\text{CH}_3\text{NH}_3\text{PbI}_3$ driving the high efficiencies in these solar cells are unknown. Herein, through femtosecond transient optical spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ heterojunctions with selective electron and hole extraction, we successfully decouple electron and hole dynamics and show clear evidence of long electron and hole transport lengths (both over 100nm). Our findings indicate that this class of materials does not suffer from the bottleneck of low collection lengths which handicap typical low temperature solution processed photovoltaic materials.

In this study, electron extraction layers (such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), C_{60}) with conduction band levels below that of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and hole extraction layers (such as Spiro-OMeTAD, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)) with valence band levels above $\text{CH}_3\text{NH}_3\text{PbI}_3$ were interfaced to $\text{CH}_3\text{NH}_3\text{PbI}_3$ to permit decoupling of the electron and hole dynamics (Fig. S1). Comparing measurements on bare $\text{CH}_3\text{NH}_3\text{PbI}_3$ against $\text{CH}_3\text{NH}_3\text{PbI}_3$ /hole acceptor bilayers and $\text{CH}_3\text{NH}_3\text{PbI}_3$ /electron acceptor bilayers enables identification of electron and hole signatures in the organic/inorganic halide. Under identical experimental conditions, the photoluminescence (PL) quantum yield of the 65 nm thick $\text{CH}_3\text{NH}_3\text{PbI}_3$ is greatly reduced when the perovskite is interfaced with an electron extracting PCBM layer or a hole extracting Spiro-OMeTAD layer (Fig. 1A). The PL intensity is quenched by a factor of 12.5 in the bilayer with Spiro-OMeTAD and by a factor of 50 in the bilayer with PCBM (Table S1). Given that the current configurations are ideal layered systems (Fig. S2 and S3), these high degrees of PL quenching, comparable to closely blended donor/acceptor system, are particularly revealing (15-19). Given a linear absorption coefficient of $5.7 \times 10^4 \text{ cm}^{-1}$ at 600 nm (Fig. 2A, S4 in supplementary material), near homogenous generation of the charge carriers in these 65 nm $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers can be ensured (20). The PL quenching is expected to originate from the charge carrier extraction across the interface (21-27). Efficient PL quenching suggests that the charge carrier diffusion length inside the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer is comparable to or longer than the layer thickness (65 nm). Correspondingly, the PL lifetimes were also significantly shortened when $\text{CH}_3\text{NH}_3\text{PbI}_3$ was interfaced with the PCBM or Spiro-OMeTAD layer (Fig. 1B) – with fitted lifetimes of $4.5 (\pm 0.3) \text{ ns}$, $0.37 (\pm 0.02) \text{ ns}$ and $0.64 (\pm 0.03) \text{ ns}$ for the $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Spiro-OMeTAD}$,

respectively. The single exponential PL decay indicates the good crystalline quality of the samples. Using the relation ($1/\tau_{\text{Heterojunction}} = 1/\tau_{\text{Perovskite}} + 1/\tau_{\text{CT}}$), the charge carrier transfer times τ_{CT} (and efficiency) can be estimated to be 0.40 ns (92%) and 0.75 ns (86%) for $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Spiro-OMeTAD}$, respectively. The slight variation between the charge carrier transfer efficiencies obtained using steady state PL (Fig. 1A and Table S1) and transient PL can be attributed to: (i) extremely fast charge carrier transfer at the interface (that cannot be monitored at the current temporal resolution); and (ii) the dependence of the steady state PL on the light reflection, scattering and refraction by the additional PCBM and Spiro-OMeTAD layers in the heterojunctions. Next, a charge carrier extraction model based on diffusion was employed to estimate the charge carrier diffusion lengths (see SM). Fig. 1C shows the dependence of the charge carrier diffusion length on the PL lifetime quenching ratios obtained from the analytical solution of the model. Assuming that charge carrier quenching occurs only at the extraction layer interface with 100% efficiency, minimum estimates of the extracted electron and hole diffusion lengths are 130 nm and 90 nm. By comparison, solution processed organic conjugated materials have typical diffusion lengths about 10 nm (21-23); thermally deposited organic molecules have typical diffusion lengths of 10 – 50 nm (24-26); and colloidal quantum dot films have diffusion lengths ~30 nm (organic cross-linked) and ~80 nm (hybrid surface passivated) (27). Thus the conservatively estimated long diffusion lengths in the low temperature solution processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ films compare favorably.

To improve the accuracy of these estimated values from the direct PL approach and obtain more details on the photo-excited charge carrier dynamics, complementary transient absorption spectroscopy (TAS) measurements were also performed (10, 17, 28-33). Due to the large absorption coefficients and the long charge carrier diffusion lengths, low pump fluence is essential to avoid extensive Auger recombination in $\text{CH}_3\text{NH}_3\text{PbI}_3$ – see Fig. S6 to S9. Fig. 2A shows the linear absorption spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ spanning the UV to near infrared (800 nm) with two distinct peaks located at 480 nm and 760 nm, in agreement with earlier publications (9-14, 20). The second absorption peak (760 nm) is attributed to the direct gap transition from the first valence band maximum (VB1) to the conduction band minimum (CB1). However, the origin of the first absorption peak (480 nm) is still unresolved. Representative TA spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and its bilayer counterparts over the same spectral region are shown in Fig. 2B to D – with two pronounced photo-bleaching (PB) bands. These long-lived PB peaks are located at almost the same spectral positions as the two absorption peaks. The PB at 480 and 760 nm are labeled as PB1 and PB2, respectively, and are attributed to state-filling (34). For 600 nm photo-excitation, it is reasonable to attribute the 760 nm PB2 band to state filling effects (which include the hole population of VB1, the electron population of CB1 and the inter-band stimulated emission) (10, 17, 28-33). However, it is not straightforward to assign the transitions associated with the 480 nm PB1 band. Given that the photo-excitation energy (of ~ 2.06 eV for 600 nm wavelength) is smaller than the energy of the PB1 peak (2.58 eV), only one of the two energy states involving this PB transition could be populated. The long-lived nature of this PB band further suggests that the populated energy level should be either VB1 or CB1 (see SM for a more detailed discussion of the assignment).

Upon selective excitation of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer, no new PB or photoinduced absorption bands are observed when the electron or hole extraction layer is present. A comparative study at the respective probe wavelengths of PB1 and PB2 would thus yield detailed information about the charge carrier dynamics. For pure $\text{CH}_3\text{NH}_3\text{PbI}_3$, the recombination dynamics at different probe wavelengths are relatively invariant over a range of pump fluences where second order effects are insignificant (Fig. S6). All these decay

transients are well-fitted with a single exponential time constant of $5.6 (\pm 0.1)$ ns, which is longer than the measured PL lifetime of $4.5 (\pm 0.3)$ ns (Table S1). As time-resolved PL cannot monitor the recombination dynamics of all the photo-excited carriers, this finding suggests that the PL lifetime in pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ is limited by the minority carrier lifetime. Correlating these PL lifetimes with the TA lifetimes of the bilayers allows us to identify the minority charge carriers.

With the PCBM (electron acceptor) layer present, both PB1 and PB2 bleaching peaks show an additional fast lifetime component of $0.37 (\pm 0.02)$ ns (Fig. 2E and 2F), which is closely matched to the measured PL lifetime. This suggests that electrons are the minority charge carriers in $\text{CH}_3\text{NH}_3\text{PbI}_3$. Since PB1 and PB2 dynamics are simultaneously affected by the electron extraction layer, the probes monitor the electron population in the CB1. For the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Spiro-OMeTAD}$ (hole acceptor) samples, only PB2 exhibits an additional fast decay lifetime of $0.59 (\pm 0.03)$ ns (Fig. 2E), which is slightly faster than the PL lifetime of $0.64 (\pm 0.03)$ ns (Table S1). This indicates that PB2 also reflects the hole population of VB1 (i.e., the transitions between VB1 and CB1). PB1 on the other hand is only related to the electron population in CB1 (i.e., the transitions between the lower valence band (VB2) and CB1) (Fig. 3C). By comparing the PB1 decays between pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$, we determined electron extraction time and efficiency values in $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ to be 0.40 ns (± 0.05) and 68%. Fig. 2E also shows that about 27% of the photo-generated electrons are possibly trapped, and therefore contribute neither to the electron extraction from $\text{CH}_3\text{NH}_3\text{PbI}_3$ to PCBM, nor to the radiative recombination. By comparing the decay at PB2 between pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Spiro-OMeTAD}$, we estimate the hole extraction time in $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Spiro-OMeTAD}$ to be $0.66 (\pm 0.05)$ ns. However, given that the TA signal at PB2 is a combination of signals from both electrons and holes, it is difficult to estimate the detailed hole extraction efficiency at this stage.

The origins of PB1 and PB2 suggest the possibility of hot holes cooling from VB2 to VB1 following excitation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ across the VB2-CB1 gap. Such hot hole cooling dynamics could be validated through varying the pump wavelengths. After 3.10 eV (400 nm) excitation, Fig. 3A shows a very fast bleach buildup for PB1 which is close to the 150 fs laser pulse duration. Subsequently, hole localization from VB2 to VB1 occurs (within ~ 0.4 ps). The decay of the PB1 transient (indicative of the depopulation of VB2) is well-matched with a concomitant rise of the bleach signal at PB2 (indicative of VB1 being populated) – both at 0.4 ± 0.1 ps. On the other hand, excitations with lower energy photons (e.g. across the VB1-CB1 gap using 2.07 eV (600 nm) pulses), do not excite carriers in VB2 and therefore, such hot hole cooling dynamics are absent (Fig. 3B). This 0.4 ps hot hole cooling is much slower than that in most organic semiconductors (~ 100 fs) (30, 35). Potentially, these hot hole energies could be efficiently extracted before the hot holes cool down to VB1 through optimizing the device configuration.

From fitting the TA decay dynamics with the diffusion model, the electron and hole diffusion coefficients were found to be 0.036 and 0.022 cm^2/s , respectively. Using these values, the electron and hole diffusion lengths (L_D) perpendicular to the film surface were calculated to be $L_D^e = 130\text{nm}$ and $L_D^h = 110$ nm where $L_D = \sqrt{D\tau_{TA}}$. As expected, the L_D^h (majority carrier diffusion length) determined here is longer than that extracted from the more direct PL approach presented earlier, which is sensitive to the minority carrier dynamics. The long transport lengths associated with $\text{CH}_3\text{NH}_3\text{PbI}_3$ are linked to its crystal structure, which consists of corner-connected PbI_6 octahedra that form a three-dimensional framework (36). Other organic/inorganic halide materials based on Sn have also displayed good charge transport properties (37, 38). The slightly shorter diffusion length of the holes compared to

the electrons is consistent with the hole's larger effective mass and larger positive space charge limited transport. Nonetheless, these values are relatively balanced as compared to typical values reported in bulk heterojunction solar cells where the electron and hole transport lengths (proportional to their mobility) differ by orders of magnitude resulting in space charge limited photocurrents (39). These balanced long charge carrier diffusion lengths would account for the remarkable performances reported for these $\text{CH}_3\text{NH}_3\text{PbI}_3$ devices. These L_D values are underestimated mainly because of the assumption that no quenching at the $\text{CH}_3\text{NH}_3\text{PbI}_3$ -quartz or -vacuum interfaces occur. The measured carrier lifetimes, τ_0 are more susceptible to the non-ideality of these interfaces in these thinner spincoated $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers, leading to smaller τ_0 and consequently shorter L_D . Measurements in more "bulk-like" samples would yield longer τ_0 and higher L_D (submicron) – Fig. 1C. From the linear absorption coefficients (Fig. 2A), the absorption lengths are $L_\alpha \sim 100$ nm (at $\lambda=500$ nm). These conservatively estimated carrier diffusion lengths measured in $\text{CH}_3\text{NH}_3\text{PbI}_3$ are comparable to the optical absorption lengths for $\lambda \leq 500$ nm, but are shorter than the absorption lengths at longer wavelengths. Increasing the optical thickness of these layers through light trapping architectures compensates for this slight mismatch – accounting for the high photoconversion efficiencies reported in these systems (9-14, 40).

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34. Typically, PB peaks in TAS could arise from Coulomb interaction or state filling of the quasi-particles. In the former case, Coulombic interaction amongst the excitons gives rise to a shift in energy of the probe beam induced transitions which occur in the vicinity of the excitons generated by the earlier pump beam. Such a phenomenon is commonly observed in quantum confined low dimensional systems or under high fluence excitation. In this mechanism, the occurrence of the PB peaks usually coincides with the occurrence of adjacent photoinduced absorption peaks due to the shift or broadening of the absorption peak. Furthermore, the PB peak positions will also shift with increasing pump fluence. The absence of photoinduced absorption peaks or pump fluence dependence of the PB peaks in these $\text{CH}_3\text{NH}_3\text{PbI}_3$ films allows us to rule out Coulomb interaction. On the other hand, state filling arises due to the changes in population of the various electronic states brought about by the initial pump beam. Hence, it will only influence probe beam induced transitions that involve electronic states with changed populations.
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Fig. 1. Photoluminescence spectroscopy. (A) Time-integrated PL spectra and (B) Time-resolved PL decay transients measured at 760 ± 10 nm for quartz/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (65 nm) (black), quartz/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (65 nm)/PCBM (red), quartz/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (65 nm)/Spiro-OMeTAD (blue) films in vacuum following excitation at 600 nm (1 KHz, 150 fs, $1.3 \mu\text{J}/\text{cm}^2$). The solid lines in (B) are the single-exponential fits of the PL decay transients. (C) A plot of exciton diffusion length vs PL lifetime quenching ratios based on equation (S5). Diffusion length is scaled in multiples of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer thickness ($L = 65$ nm).

Fig. 2. Steady-state and transient absorption spectroscopy. (A) UV-Vis absorbance spectrum for pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer. (B)-(D) Differential transmission spectra for $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$, $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Spiro-OMeTAD}$ films in vacuum following excitation at 600 nm (1 KHz, 150 fs, $13 \mu\text{J}/\text{cm}^2$). Red spectrum (1 ps), Green spectrum (100 ps), Blue spectrum (500 ps), Cyan spectrum (1 ns). Normalized bleaching kinetics at (E) 480 nm and (F) 760 nm for the films in vacuum following excitation at 600 nm (1 KHz, 150 fs, $1.3 \mu\text{J}/\text{cm}^2$).

Fig. 3. Early time dynamics. Normalized bleaching kinetics at 480 nm and 760 nm in short time range show the inter-valence band hot hole cooling for $\text{CH}_3\text{NH}_3\text{PbI}_3$ film (in vacuum) following excitation at (A) 400 nm ($1 \mu\text{J}/\text{cm}^2$) and (B) 600 nm ($1.3 \mu\text{J}/\text{cm}^2$). (C) A schematic illustrating the hot hole cooling and charge recombination within $\text{CH}_3\text{NH}_3\text{PbI}_3$ and charge separation at the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Spiro-OMeTAD}$ interfaces. The approximate positions of VB1 and VB2 were obtained from the TA measurements.

Supplementary Materials

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Materials and Methods

Figures S1-S9

Tables S1

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