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Advanced Energy Materials 2017,
<https://doi.org/10.1002/aenm.201602349>

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Date deposited:

25/04/2017

Embargo release date:

17 February 2018

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DOI: 10.1002/ ((please add manuscript number))

Article type: Full Paper

Charge Transfer from Methylammonium Lead Iodide Perovskite to Organic Transport Materials: Efficiencies, Transfer Rates and Interfacial Recombination

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Keywords: perovskite, charge transfer, TRMC, transport materials, solar cells

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Perovskite-based photovoltaics have been rapidly developed, with power conversion efficiencies exceeding 22%. For rational design of efficient and stable perovskite solar cells, it is important to understand processes occurring at the perovskite/transport material (TM) interface, such as charge transfer and interfacial recombination. In this work, Time-Resolved Microwave Conductivity measurements are performed to investigate interfacial processes for methylammonium lead iodide and various organic TMs. A global kinetic model is developed to describe both the dynamics of excess charges in the perovskite layer and transfer to charge-specific TMs. From the obtained charge transfer rates, we deduce the extraction efficiencies. We conclude that for state-of-the-art materials, such as Spiro-OMeTAD and PCBM, charge extraction is not significantly affected by intra-band gap traps. That is, for trap densities under 10^{15} cm^{-3} , the trapping rates ($<10^7 \text{ s}^{-1}$) are substantially lower than the transfer rates (typically $\sim 10^8 \text{ s}^{-1}$). Finally, our results show that transfer rates to C60, PCBM, EDOT-OMeTPA and Spiro-OMeTAD are sufficient to outcompete second order recombination under excitation

densities representative for illumination by AM1.5. These results pave the way for rational design of perovskite-based solar cells with balanced extraction of charges, which essential for avoiding accumulation of charges at one of the electrodes.

1. Introduction

Solar cells employing metal halide perovskites as light absorbers have undergone a tremendous development over the past years, resulting in photovoltaic devices with record efficiencies exceeding 22%.^[1–3] The impressive progress in device efficiency is mainly due to (i) optimizing experimental procedures to obtain perovskite materials with improved crystallinity, (ii) adjusting the perovskite composition and (iii) investigating different transport materials. However, it remains a major challenge to eliminate the hysteresis in the photovoltaic current-voltage scans, thereby stabilizing perovskite-based solar cells. Recently, it was shown that hysteresis in perovskite-based solar cells is highly dependent on the choice of transport materials (TM), suggesting that device performance is limited by charge accumulation at the interfaces.^[4,5] Hence, better understanding of the perovskite/TM interfaces is critical for rational design of stable perovskite-based solar cells with minimum hysteresis and improved device lifetimes.

Interestingly, in contrast to the substantial progress that has been made in understanding the dynamics of photo-generated charges in the photo-active metal halide perovskite,^[6,7] there are only a handful of reports investigating the kinetics of charge transfer from perovskite to charge-specific TMs.^[8–12] We have previously proposed that injection of charges can be in competition with recombination pathways in the perovskite layer, in particular if the perovskite is unintentionally doped.^[9] Other groups have extracted transfer rates^[8] or yields^[13] from global analysis of spectroscopic data. However, a quantitative description accounting both for the dynamics of charges in the perovskite itself and the transfer to charge-specific electrodes is still lacking.

In this work, we use Time-Resolved Microwave Conductivity (TRMC) measurements to reveal the charge carrier transfer and recombination pathways in bilayer systems of thin MAPbI₃ films and charge-selective transport materials (TM). First, we prepared smooth, homogeneous MAPbI₃ layers using sequential physical vapour deposition (PVD).^[14–16] Via this route, multiple MAPbI₃ films with identical optoelectronic properties can be made, which enables for direct comparison between different samples. Then, various organic electrodes were spin-coated on top of the MAPbI₃ films, so that we could compare the photo-physical processes in a bilayer to those in a neat perovskite.^[9] Both the frequently used hole transporting material (HTM) Spiro-OMeTAD and the recently reported low-cost alternatives H101^[17] and EDOT-OMeTPA^[18] were investigated. Similarly, state-of-the-art PCBM and C60 were compared to less commonly used electron transport materials (ETM's) such as ICBA^[19] and bis-PCBM.

Interestingly, we find that on the timescale of our TRMC experiment, charge transfer of electrons or holes occurs independently of excitation wavelength and illumination side, indicating that this process is not limited by charge diffusion in perovskite films with thicknesses of a few hundred nanometers. We introduce a global kinetic model that implements charge carrier generation, various recombination pathways in the perovskite layers and in addition, the transfer rates to charge-selective TMs. First, the dynamic parameters, including mobilities and rate constants for band-to-band recombination and trapping, are revealed for the neat perovskite layer, as previously described.^[20,21] After depositing the TM layer, the same set of kinetic parameters plus an additional rate constant is used to describe the transfer of charges. Hence, we find the rates of charge transfer and interfacial recombination for a number of different organic TMs. Additionally, this model enables us to separate the electron and hole mobilities and to deduce the charge collection efficiency as a function of charge carrier density (*i.e.*, illumination intensity). We find that at low densities, charge transfer can be in competition with charge immobilization due to the

presence of traps, whereas second order recombination in the perovskite dominates over extraction at higher densities. Most importantly, these results demonstrate that transfer of charges is optimized when the transfer rates exceed the trapping rates, which is the case for *e.g.* Spiro-OMeTAD and PCBM.

2. Results and Discussion

To study the transfer of charges from MAPbI₃ to various organic TMs, the charge carrier dynamics in neat perovskite films were directly compared to bilayer systems. The different types of sample configurations are schematically shown in **Figure 1**. A short (3.5 ns fwhm) laser pulse is used to excite the samples through the quartz substrate, thereby generating free charges in the MAPbI₃ layer. As previously reported, these charges decay over time by trap-assisted and/or second order electron-hole recombination.^[20,22] When an ETM (or HTM) is deposited on top of the MAPbI₃, electrons (holes) are extracted and consequently, these can recombine via the interface with holes (electrons) that remained in the MAPbI₃.

Using MAPbI₃ layers with identical optoelectronic properties, the charge carrier dynamics and transfer to the electrodes was investigated quantitatively. The initial location of charges was manipulated by varying the excitation wavelength. **Figure 2a** shows the charge carrier generation profile in MAPbI₃ for excitation wavelengths of 300, 600 and 780 nm, calculated using the experimentally determined absorption coefficients (see **Figure S1**). At $\lambda = 300$ nm, the penetration depth ($1/\alpha$) of light is only 30 nm and hence, photo-excitation is concentrated close to the illuminated surface. On the other hand, at $\lambda = 780$ nm, the lower absorption coefficient results in a diluted, more homogeneous excitation profile. **Figure 2b** shows the normalized photo-conductance ΔG in a thin (~200 nm) vapour-deposited MAPbI₃ film (see **Figures S2 to S4**)^[14–16,23] as a function of time after pulsed illumination ($\sim 10^{10}$ absorbed photons/cm² per pulse), recorded using the TRMC technique.^[24] Given that ΔG provides a measure for the density of free mobile charges, its initial rise is due to charge generation by

the laser pulse, whereas its reduction over time can be directly related to immobilization of charges by *e.g.* trapping or recombination. As shown in **Figure 2b**, the signal has reduced to half its initial value within 200 ns for an initial charge carrier density of $5 \times 10^{14} \text{ cm}^{-3}$. Interestingly, this is independent of the excitation wavelength λ . Similar TRMC results were obtained for excitation from the front side (*i.e.* through the organic layer) and from the back side (see **Figure S5**). Thus, the results in **Figure 2b, 2c and S5** show that the timescale for recombination does not depend on the initial distribution of charges, which indicates that transport occurs on a much faster timescale than recombination.

To gain more insight in the charge carrier dynamics in MAPbI₃ and the charge collection by TM layers, we deposited Spiro-OMeTAD on top of the perovskite and repeated the TRMC measurements. The samples were excited through the quartz substrate and thus, in this case, varying the excitation wavelength changes the distance of charge carriers to the MAPbI₃/Spiro-OMeTAD interface. The change in conductance is given by:

$$\frac{\Delta P(t)}{P} = -K\Delta G(t) \quad (1)$$

Then, the product of the yield of free charges ϕ and their mobility $\Sigma\mu$ can be calculated from the maximum ΔG :

$$\frac{\Delta G_{max}}{\beta e I_0 F_A} = \phi \Sigma\mu \quad (2)$$

where $\Sigma\mu$ is the sum of the electron and hole mobilities ($\mu_e + \mu_h$). Hence, all light-induced mobile charges contribute to the TRMC signal, however scaled by their mobility. Since the electron and hole mobilities in organic compounds are much smaller than in MAPbI₃, we can assume that the charges injected into the TM layers do not contribute significantly to ΔG .

Thus, the traces in **Figure 2c** originate from free charges remaining in the perovskite. In contrast, the lifetime of mobile charges is substantially extended in the bilayer configuration with respect to the neat perovskite, as shown in **Figures 2b and 2c**. We attribute this to injection of holes into the Spiro-OMeTAD, which reduces the probability of electrons remaining in MAPbI₃ to recombine with holes and consequently, enhances their lifetime. Interestingly, similar to the neat perovskite, we find that the decay in the bilayer hardly changes with the excitation wavelength. In other words, photo-generated holes can diffuse effectively through the perovskite layer over a distance of at least 150 nm and reach Spiro-OMeTAD. Furthermore, the observation that the electron lifetime in MAPbI₃ is shorter in the presence of holes (**Figure 2b**) confirms our previous conclusions that higher order electron-hole recombination dominates the decay in the neat perovskite.^[21] We note that, although the absolute lifetimes are dependent on the sample preparation and excitation conditions, bilayers prepared from vapour-deposited and spin-coated samples show similar trends (see **Figure S6**). To study the electron-hole recombination pathways in more detail, we performed TRMC measurements as a function of the initial charge carrier density. **Figures 3a and 3b** show ΔG normalized for the number of absorbed photons in MAPbI₃ (**Figure 3a**) and MAPbI₃/Spiro-OMeTAD (**Figure 3b**) for charge densities ranging from 7×10^{13} to 10^{16} cm^{-3} . In the neat perovskite, the charge carrier decay becomes faster at higher densities, which is typical for higher order electron-hole recombination, as discussed previously.^[20] Importantly, the opposite trend is observed when holes are transferred to Spiro-OMeTAD: the electron lifetime is shorter at low densities and vice versa. In fact, these results suggest the presence of a limited density of electron traps. That is, if the density of electron traps exceeds the density of free electrons, the latter are likely to be immobilized into trap states resulting in a faster decay. On the other hand, if the electron density exceeds the trap density, their lifetime will be enhanced, provided that there are no holes to recombine with (**Figure 3b**). Hence, TRMC measurements using extraction layers enables us to identify the nature of trap states (*i.e.*

electron or hole traps), which is not possible with *e.g.* photoluminescence (PL) measurements.

Finally, considering that the signal in **Figure 3b** originates primarily from electrons remaining in MAPbI₃, we can conclude that the contribution of the electrons (μ_e) to the sum of the mobilities $\Sigma\mu$ (**Figure 3a**) is larger than the contribution of μ_h .

Analogous to our previous work,^[20] we use a kinetic model to obtain quantitative information from the intensity-dependent TRMC traces; see **Figure 4**. This model not only includes processes occurring in MAPbI₃ (black, see also Refs.^[20,22]), but is extended to account for the additional pathways introduced by the electron or hole transport material (red).^[9] Upon absorption of light ($h\nu$), electrons (n_e) are excited to the conduction band (CB), leaving holes (n_h) in the valence band (VB). The laser pulse (G_C) initially generates equal densities of excess electrons ($\Delta n_{CB} = \Delta n_e$) and holes ($-\Delta n_{VB} = \Delta n_h$), which depend on the intensity of absorbed photons. Since the exciton binding energy of several meV is lower than the thermal energy at room temperature,^[25] we assume that every absorbed photon yields a single free electron and hole.^[26] In MAPbI₃, the electrons can recombine with holes via second order recombination (k_2) or traps (k_T and k_R). Additionally, in the presence of an ETM, electrons can be extracted (k_e) and recombine via the interface with holes (k_h). Vice versa, if the TM is hole-selective, $k_h \gg k_e$ and thus k_h represents hole extraction. The time-dependent change in the electron densities in the CB, VB, trap states (N_T) and TM are described by the coupled differential **Equations 3 to 6**, respectively.

$$\frac{dn_{CB}}{dt} = \frac{dn_e}{dt} = G_C - k_2 n_e (n_h + p_0) - k_T n_e (N_T - n_T) - k_e n_e \quad (3)$$

$$\frac{dn_{VB}}{dt} = -\frac{dn_h}{dt} = -G_C + k_2 n_e (n_h + p_0) + k_R n_t (n_h + p_0) + k_h n_h \quad (4)$$

$$\frac{dn_t}{dt} = k_T n_e (N_T - n_T) - k_R n_t (n_h + p_0) \quad (5)$$

$$\frac{dn_{TM}}{dt} = k_e n_e - k_h n_h \quad (6)$$

We used the kinetic model shown in **Figure 4** to globally fit the experimental TRMC data,^[20] which are added as dotted lines in **Figures 3a and 3b**. As shown in **Figure 3**, excellent agreement could be obtained between the modelled and the experimental traces. Remarkably, except for hole injection (k_h), the same kinetic parameters could be used to describe both the neat perovskite and the MAPbI₃/Spiro-OMeTAD bilayer (see **Table 1**). Most importantly, the density-dependent lifetime of electrons in the absence of holes (MAPbI₃/Spiro-OMeTAD, **Figure 3b**) enables us to accurately determine the trapping parameters N_T and k_T .

Consequently, we find that $k_2 = 2.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $k_T = 6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and that the trap density is exceptionally low ($3 \times 10^{14} \text{ cm}^{-3}$), similar to spin-coated MAPbI₃ prepared from PbCl₂.^[20] The density of dark holes (p_0) is $4 \times 10^{14} \text{ cm}^{-3}$, which is in line with experimental findings.^[27] Additionally, the only difference between the traces in **Figure 3a and 3b** is the injection of holes, from which we deduce that holes are transferred from MAPbI₃ to Spiro-OMeTAD with $k_h = 8 \times 10^8 \text{ s}^{-1}$. As there is no signature of interfacial recombination within the timeframe studied, we conclude that $k_e < 2 \times 10^4 \text{ s}^{-1}$.

Finally, whereas we previously had to assume on basis of the effective mass the relative contributions of electrons and holes to the sum of mobilities, these can now be separately determined. Hence, in contrast to previous assumptions, we find that the electron mobility is $30.5 \text{ cm}^2/\text{Vs}$, while the hole mobility is $6.5 \text{ cm}^2/\text{Vs}$. Considering that the kinetic model also separates the electron and hole lifetimes, the diffusion lengths L_D can now be individually estimated for both charges using $L_D = (D \tau_{1/2})^{1/2}$ with $D = \mu k_B T / e$ and $\tau_{1/2}$ the half lifetime. We estimate that at charge densities comparable to illumination with AM1.5, the electron diffusion length is $1.8 \text{ }\mu\text{m}$, and $0.8 \text{ }\mu\text{m}$ for the holes. Thus, although the electrons are more

mobile than the holes, both diffusion lengths are larger than the $\sim 0.4 \mu\text{m}$ MAPbI₃ thickness required for sufficient light absorption and thus, both charges are mobile enough to be efficiently collected in a device. Finally, these mobilities corresponding to electron and hole diffusion coefficients of $0.78 \text{ cm}^2/\text{s}$ and $0.16 \text{ cm}^2/\text{s}$, respectively, explain the independence of excitation wavelength as presented in **Figure 2b and 2c**. That is, it takes $\sim 3 \text{ ns}$ for the holes to diffuse throughout the 200 nm film, which is below the time response of our measurement.

The above approach enabled us to accurately determine the mobilities and recombination pathways of electrons and holes in MAPbI₃, which we used to obtain transfer rates for the other TMs investigated. **Figure 5** shows TRMC traces recorded for bilayers of MAPbI₃ and the HTMs: H101 (a) and EDOT-OMeTPA (b), together with the ETMs: PCBM (c), MAPbI₃/C60 (d), MAPbI₃/ICBA (e) and MAPbI₃/bis-PCBM (f). The fits to the experimental data as detailed above are added as dotted lines. We note that the perovskite-related mobilities and recombination rates were fixed for all the bilayer systems, leaving k_e and k_h as the only variables. The results are listed in **Table 2**.

Looking at the experimental data for the HTMs investigated, we observe that lifetimes are extended when H101 is spin-coated on top of MAPbI₃. In contrast to Spiro-OMeTAD however, the decay in MAPbI₃/H101 shows higher order recombination effects within the first 100 ns . This suggests that injection into H101 is slower than for Spiro-OMeTAD and therefore, initially in competition with second order recombination in MAPbI₃. At longer timescales however, the holes have transferred to H101 and the lifetime of the remaining electrons follows the same trend as for Spiro-OMeTAD. As shown in **Figure 5a**, this behaviour can indeed be modelled using a lower k_h : both the experimental and fitted traces cross over between 100 and 200 ns (see also **Figure S7**). Additionally, the shorter electron lifetime in MAPbI₃/H101 suggests a higher value for interfacial recombination k_e (see **Figure 5a and Table 1**).

For MAPbI₃/EDOT-OMeTPA, as shown in **Figure 5b**, the decay is substantially faster than in the neat perovskite, *i.e.* in this bilayer configuration both electrons and holes have recombined within a few nanoseconds. Consequently, we find that holes are transferred with a rate constant of $8 \times 10^8 \text{ s}^{-1}$, followed by electron immobilization with $k_e = 1.5 \times 10^8 \text{ s}^{-1}$. This rapid quenching of mobile electrons at the MAPbI₃/EDOT-OMeTPA interface could be due to recombination with injected holes and/or trapping of electrons at the interface. Similarly, we find that for all the ETMs shown in **Figures 5c to 5f**, electron injection is followed by rapid immobilization of holes, as already reported for MAPbI₃/PCBM before.^[9,28] This is characteristic of the interface between MAPbI₃ and all the fullerene-related ETMs studied, since we observed this independently of the MAPbI₃ preparation method and the thickness of the ETM (**Figure S8a**). Using the kinetic model from **Figure 4**, we find interfacial recombination rates in the order of $10^6 - 10^7 \text{ s}^{-1}$. However, we cannot exclude that this represents trapping of holes at the MAPbI₃/ETM interface rather than recombination with injected electrons (**Figure S8b**). We note that interfacial recombination at the ETM interface is *not necessarily* a limiting factor for photovoltaic performance, as long as the holes are efficiently collected at the other TM. However, in the case of comparable rate constants for injection and interfacial recombination, as for *e.g.* EDOT-OMeTPA, this will be detrimental for device performance.

Interestingly, comparing the injection rates listed in **Table 2**, we find that electron transfer from MAPbI₃ to ICBA or bis-PCBM is one order of magnitude slower than injection into the other ETMs investigated. This can be understood considering that the LUMO levels of ICBA and bis-PCBM are located above the CB of MAPbI₃, since their electron affinities are 0.2 eV lower than that for PCBM.^[29] Although this could result in a higher V_{OC} ,^[19] its band alignment might not favor electron extraction, which explains the relatively low transfer rate in MAPbI₃/ICBA. These results suggest that other electron recombination pathways such as trapping or recombination with holes could be competing with injection into ICBA. That is, if

the trapping rate ($\sim k_T N_T$) and/or the higher order recombination rate ($\sim k_2 n_e n_h$) is in excess of the injection rate of ($1.2 \times 10^7 \text{ s}^{-1}$), this will dominate over injection. However, in high quality films the trapping rate ($\sim k_T N_T$) is on the order of 10^6 s^{-1} and hence, too small to impede injection.

Using the rate constants for injection as well as the additional recombination pathways in the perovskite, we can now quantify the yield of electron extraction ϕ_e as a function of n_e .

$$\phi_e = \frac{k_e n_e}{k_e n_e + k_2 n_e (n_h + p_0) + k_T n_e (N_T - n_t)} \quad (7)$$

which is defined as the ratio between the electron injection rate and the total recombination rate for electrons. Similarly, the hole extraction yield ϕ_h is given by:

$$\phi_h = \frac{k_h n_h}{k_h n_h + k_2 n_e (n_h + p_0) + k_R n_t (n_h + p_0)} \quad (8)$$

Figures 6a and **6b** show ϕ_e and ϕ_h , respectively, as a function of the excitation density, using the kinetic parameters listed in **Table 1** and **2**. Note that AM1.5 illumination under open circuit conditions leads to charge carrier densities on the order of 10^{15} cm^{-3} .^[30] **Figure 6a** shows that at low charge carrier densities, ϕ_e is close to unity for PCBM and C60, which can be understood considering that the injection is fast enough to overcome trapping (*i.e.*, $k_e \gg k_T N_T$). On the other hand, in view of the lower injection rates, electron injection into ICBA and bis-PCBM is in competition both with trapping and second order recombination. Therefore, the transfer yield will always be less than 80% even if all trap-assisted recombination is eliminated (*i.e.* for $k_e \sim 10^7 \text{ s}^{-1}$ and $k_2 \sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). Finally, for all ETMs, ϕ_e drops down when the density increases. This decrease in ϕ_e is due to second order recombination effects ($\sim k_2 n_e n_h$), which start to dominate over injection at high charge carrier

densities. The same trends are observed for the HTMs (**Figure 6b**): ϕ_h is close to unity at low densities and decreases at increasing densities. Furthermore, ϕ_h remains higher for Spiro-OMeTAD than for H101, which can be understood considering that k_h is lower for the latter. Obviously, electron injection into PCBM could also be impeded by the presence of traps, but only if the trap densities are much higher, *e.g.* less than 50% of the electrons are injected if N_T would be $5 \times 10^{16} \text{ cm}^{-3}$ (see **Figure 6c**).^[20] Similarly, in samples prepared via different routes, the traps could be hole-selective and ϕ_h could be lower since trapping of holes competes with transfer to the HTM. Finally, considering that illumination with AM1.5 results in charge densities in the order of $10^{15} - 10^{16} \text{ cm}^{-3}$, these results show that transfer rates to C60, PCBM, EDOT-OMeTPA and Spiro-OMeTAD are high enough to outcompete second order recombination.

3. Conclusion

In this work, we investigated the transfer of optically excited charge carriers from MAPbI₃ to different organic TMs. The TRMC technique was used to study the charge carrier dynamics both in neat MAPbI₃ and bilayers of MAPbI₃ with an ETM or HTM on top. We proposed a global kinetic model, which we used to quantify the recombination dynamics in the MAPbI₃ as well as the additional pathways introduced by the presence of an ETM or HTM. Hence, we were able to deduce rate constants for extraction and interfacial recombination for several organic TMs. Interestingly, we find that both for the state-of-the-art HTM Spiro-OMeTAD and the low-cost alternatives H101 and EDOT-OMeTPA, holes are efficiently collected. However, for the latter this is followed by rapid recombination at the MAPbI₃/EDOT-OMeTPA interface, which is expected to limit device performance. For the ETMs, we find that injection into PCBM and C60 is substantially more efficient than into ICBA and bis-PCBM, which might be due to the lower electron affinity of the latter two. Finally, we find that intra-band gap traps do barely affect injection, as long as the trapping rate ($\sim k_T N_T$) is

substantially lower than the transfer rates (typically $\sim 10^8 \text{ s}^{-1}$), which is the case for trap densities less than 10^{15} cm^{-3} .

4. Experimental Section

Sample preparation

Thin films (200 nm) of MAPI on quartz substrates were prepared by sequential physical vapour deposition of the precursors PbI_2 and freshly synthesized MAI (as described elsewhere) in a stoichiometric ratio. Therefore, an adapted evaporation machine (ATC Orion 4 – AJA International, Inc.) with Deposition Controller (SQC-310 Inficon) and Thermal Evaporation Controller (TEC-15A) was used. MAI synthesized using standard procedures and commercially available lead iodide ($\text{PbI}_2 \geq 99\%$, Sigma Aldrich) were put into quartz crucibles, which were positioned in the vacuum chamber after which the pressure was reduced to 10^{-5} - 10^{-6} mbar. For each deposition, eight plasma-cleaned quartz substrates were introduced in the vacuum chamber. Consequently, the crucible containing the PbI_2 precursor was heated to 220-240°C until the desired deposition rate of 0.5 Å/s was reached, as indicated by a quartz microbalance. The MAI was heated to 60-80°C to reach a rate of 1.3 Å/s. Then, MAPbI_3 was obtained by alternating deposition of 1 nm PbI_2 and 2 nm MAI (with 16 seconds in between), which was repeated until a total thickness of 200 nm was reached. Finally, the films were annealed at 100°C for 1 hour. The bilayers were prepared by spin-coating the HTMs and ETMs on top of the vapor-deposited MAPI films. EDOT-OMeTPA was synthesized according to previously reported procedures,^[18] while H101 and Spiro-OMeTAD were obtained from commercial sources. EDOT-OMeTPA was spin coated from a 15 mg/mL chlorobenzene solution. A 75 mg/mL chlorobenzene solution was prepared for H101 and Spiro-OMeTAD. Dopants were added to all HTM solutions: 10 µL/mL 4-*tert*-butylpyridine (t-BP) and 30 µL/mL of a lithium bistrifluoromethylsulfonamide (Li-TFSI) solution (173 mg/mL Li-TFSI in acetonitrile solution). While rotating the sample at a speed of 150 rpm, 100

μL EDOT-OMeTPA solution was deposited on top of the thin film MAPI, after which the rotational speed was increased to 1200 rpm for 45 s. H101 and Spiro-OMeTAD were spincoated by depositing 60 μL of the solution while rotating the sample at 1500 rpm for 45 s. This resulted in HTM thicknesses of 40 nm for EDOT-OMeTPA and 250 nm for Spiro and H101.^[18] MAPI/HTM bilayers were stored overnight with 30% relative humidity in order to let the HTM oxidize.

For the ETMs, PCBM, bis-PCBM and ICBA, 35 mg ETM/mL chlorobenzene solutions were prepared. From these solutions, 60 μL was deposited on the sample while rotating at 3000 rpm for 45 s. The thickness of the PCBM layer was found to be around 70 nm. Layers of the other ETMs were estimated to have similar thickness.

Optical Characterization

Absorption and transmission spectra were recorded with a Perkin-Elmer Lambda 1050 spectrophotometer equipped with an integrated sphere. The thin films were placed in front of the sphere to measure the fraction of transmitted light (F_T) and under an angle of 10° inside the sphere to detect the total fraction of reflected and transmitted photons (F_{R+T}). From here, we calculated the fraction of absorbed light (F_A):

$$F_A = 1 - F_{T+R} \quad (9)$$

The fraction of reflected light (F_R) was determined from:

$$F_R = 1 - F_A - F_T \quad (10)$$

The absorption coefficient α is often calculated from the transmission spectrum using:

$$\frac{I_L}{I_0} = e^{-\alpha L} \quad (11)$$

Where I_L/I_0 equals F_T for a sample of thickness L with negligible reflection. However, since $\text{CH}_3\text{NH}_3\text{PbI}_3$ films are highly reflective, α was obtained from:

$$\frac{F_T}{1-F_R} = e^{-\alpha L} \quad (12)$$

Photoconductance measurements

The thin films on quartz substrates were placed in a sealed resonance cavity inside an N_2 -filled glovebox. The Time Resolved Microwave Conductivity (TRMC) technique was used to measure the change in microwave (8-9 GHz) power after pulsed excitation (repetition rate 10 Hz) of the samples at different excitation wavelengths.^[24] The bilayers were illuminated both from the front side (through the electrode) and the back side (through the quartz). Neutral density filters were used to vary the intensity of the incident light. The photo-excitation-induced change in microwave power is related to the change in conductance ΔG by a sensitivity factor K :

$$\frac{\Delta P(t)}{P} = -K\Delta G(t) \quad (13)$$

The rise of ΔG is limited by the width of the laser pulse (3.5 ns FWHM) and the response time of our microwave system (18 ns). The slow repetition rate of the laser of 10 Hz ensures full relaxation of all photo-induced charges to the ground state before the next laser pulse hits the sample. With equation 12, the product of yield ϕ and mobility ($\mu_e + \mu_h$) was calculated from the maximum change in photo-conductance ΔG_{max} :

$$\varphi \Sigma \mu = \frac{\Delta G_{\max}}{I_0 \beta e F_A} \quad (14)$$

Here, I_0 is the number of photons per unit area per pulse, β is the ratio of the inner dimensions of the microwave cell, e the elementary charge and F_A the fraction of light absorbed by the sample at the excitation wavelength. Before and during the photo-conductance measurements, the samples were not exposed to moisture and air to prevent degradation

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the Netherlands Organization for Scientific Research (NWO) under the Echo grant number: 712.014.007. The authors thank Davide Bartesaghi for critical reading of this manuscript.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Figure 1. Schematic overview of the sample configurations investigated. Samples are illuminated with a laser pulse through the quartz, generating free electrons (black spheres) and holes (white spheres). In the neat perovskite (left), their density will decrease over time due to second-order (k_2) or trap-assisted recombination. In the presence of an electron transport material (ETM, middle), electrons can be extracted (k_e) and recombine with holes via the interface (k_h). Similarly, a hole transport material (HTM, right) extracts the holes (k_h) which can recombine via the interface (k_e) with electrons.

Figure 2. (a) Charge carrier generation profile as a function of excitation wavelength, calculated using the experimentally determined absorption coefficients (see also Figure S1). (b-c) Normalized time-resolved photo-conductance in a thin (~200 nm) MAPbI₃ film (b) and in a bilayer of MAPbI₃ and Spiro-OMeTAD (c) for a fluence of 10^{10} cm⁻² absorbed photons (I_0F_A) per pulse at excitation wavelengths of 300 nm, 600 nm and 780 nm. Since the fraction of absorbed photons (F_A) is wavelength-dependent, the laser intensity I_0 was adjusted in order to obtain the same product of I_0F_A . Hence, the total number of photo-excited charges is similar, however their initial distribution differs (see **Figure 2a**). Whereas for $\lambda = 780$ nm, excitation occurs nearly homogeneous throughout the MAPbI₃ layer, for $\lambda = 300$ nm charges are generated predominantly ~ 150 nm away from the MAPbI₃/Spiro-OMeTAD interface.

Figure 3. Time-Resolved Microwave Conductivity (TRMC) traces recorded at initial charge carrier densities ranging from 7×10^{13} to $3 \times 10^{16} \text{ cm}^{-3}$ ($\lambda = 600$) for neat MAPbI₃ (a) and MAPbI₃/Spiro-OMeTAD illuminated through the perovskite (b).

Figure 4. Kinetic model of processes occurring in a bilayer of MAPbI₃ perovskite and an organic electron transport material (ETM) or hole transport material (HTM). Electrons (black spheres) and holes (white spheres) are selectively generated in the perovskite film upon absorption of light ($h\nu$) with $\lambda = 600 \text{ nm}$. In the neat perovskite, electrons can recombine with holes via second order band-to-band recombination (k_2), or get trapped (trap density N_T , trapping rate k_T) and recombine with holes via k_R .^[20,22] Both k_2 and k_R are enhanced by the presence of a limited number of dark holes p_0 .^[27,31] In the presence of an organic transport layer, electrons and holes can be injected via k_e and k_h , respectively, which provides a pathway competitive to recombination in the perovskite.^[9] Note that for an ETM, $k_e \gg k_h$ and vice versa.

Figure 5. Time-Resolved Microwave Conductivity (TRMC) traces for MAPbI₃/H101 (a) and MAPbI₃/EDOT-OMeTPA (b) MAPbI₃/PCBM (c), MAPbI₃/C60 (d), MAPbI₃/ICBA (e) and MAPbI₃/bis-PCBM (f) recorded at initial charge carrier densities ranging from 10¹⁴ to 3 x 10¹⁶ cm⁻³ (at λ = 600). The dotted lines are fits to the experimental data (solid lines), using the model shown in **Figure 4** and the kinetic parameters listed in **Tables 1 and 2**.

Figure 6. (a-b) Injection yield as a function of charge carrier density for different ETMs (a) and HTMs (b), using **Equations 7** (a) and **8** (b) and the kinetic parameters from **Tables 1** and **2**. As we extracted from the TRMC measurements, trapping of electrons ($\sim k_T N_T$) is in competition with extraction (k_e), which can lower the extraction yield. This is especially relevant for ETMs with relatively low injection rates such as ICBA. In general, both ϕ_e and ϕ_h decrease when the charge carrier density increases ($> 10^{16} \text{ cm}^{-3}$), since higher order recombination starts to dominate over injection. (c) Electron transfer yield from MAPI to PCBM as a function of the density of electron traps (N_T).

Table 1. Kinetic parameters for recombination processes in MAPbI₃: the exact same parameters were used to describe both the neat perovskite (**Figure 3a**) and the bilayer systems (**Figure 3b** and **Figure 5**).

k_T (cm ³ s ⁻¹)	k_2 (cm ³ s ⁻¹)	k_R (cm ³ s ⁻¹)	N_T (cm ⁻³)	p_0 (cm ⁻³)	μ_e (cm ² V ⁻¹ s ⁻¹)	μ_h (cm ² V ⁻¹ s ⁻¹)
6.0×10^{-9}	2.8×10^{-9}	5.0×10^{-11}	3.0×10^{14}	4.0×10^{14}	30.5 ± 0.5	6.5 ± 0.5

Table 2. Rate constants for electron (k_e) and hole (k_h) transfer from MAPbI₃ to different HTMs and ETMs. Note that for the HTMs, k_h describes extraction and k_e represents interfacial recombination, while the opposite is valid for the ETMs.

	k_h (s ⁻¹)	k_e (s ⁻¹)
MAPbI ₃	0	0
HTMs		
MAPbI ₃ /EDOT-OMeTPA	8.0×10^8	1.5×10^8
MAPbI ₃ /Spiro-OMeTAD	4.0×10^8	2.0×10^4
MAPbI ₃ /H101	1.0×10^8	1.8×10^6
ETMs		
MAPbI ₃ /C60	1.2×10^7	3.0×10^8
MAPbI ₃ /PCBM	1.5×10^7	3.0×10^8
MAPbI ₃ /bis-PCBM	1.8×10^6	1.5×10^7
MAPbI ₃ /ICBA	2.0×10^6	1.2×10^7

Keywords: perovskite, charge transfer, TRMC, transport materials, solar cells

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Charge Transfer from Methylammonium Lead Iodide Perovskite to Organic Transport Materials: Efficiencies, Transfer Rates and Interfacial Recombination

MAPbI₃/Spiro-OMeTAD

Supporting Information

Charge Transfer from Methylammonium Lead Iodide Perovskite to Organic Transport Materials: Efficiencies, Transfer Rates and Interfacial Recombination

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Figure S1: Semi-logarithmic plot of the absorption coefficient of MAPbI₃. As detailed in Equation 12 in the main text, the incident light is corrected for reflection.

Figure S2: (a) Schematic representation of sequential physical vapour deposition from MAI and PbI₂ powders (see experimental methods). The MAI powder is heated to 60-80°C, while the PbI₂ is heated to 220-240°C. Then, MAPbI₃ is obtained by alternating deposition of 1 nm PbI₂ and 2 nm MAI until the desired thickness is obtained. (b-c) Fraction of light absorbed (b) and reflected (c) as a function of thickness.

Figure S3: X-Ray Diffraction (XRD) pattern using Co Kα radiation ($\lambda = 1.54 \text{ \AA}$) for a 200 nm thick vapour-deposited MAPbI₃ film. The primary reflections are the <110> and <220>.

showing that the films are highly oriented. A slight excess of PbI_2 was found to be present, as indicated by the reflection at 14.2° .

Figure S4: Scanning Electron Microscopy (a) and Atomic Force Microscopy (b) image of a vapour-deposited MAPbI_3 film, showing that the size of crystalline domains is on the order of several hundred nm's.

Figure S5: Photo-conductance as a function of time after excitation from the back side (through the quartz) (a) and the front side (through the Spiro-OMeTAD) (b) for 10^9 to 8×10^{10} photons/ cm^2 ($\lambda = 600$).

Figure S6: Normalized photoconductance as a function of time after excitation for neat MAPbI_3 (red), $\text{MAPbI}_3/\text{EDOT-OMeTPA}$ (black) and $\text{MAPbI}_3/\text{Spiro-OMeTAD}$ (blue) for spin-coated (a) and vapour-deposited (b) MAPbI_3 films. Although the sample-to-sample variation is observed in the absolute lifetimes, the same trends are observed. That is, the lifetime of the electrons remaining in MAPbI_3 is extended when the holes are transferred to Spiro-OMeTAD, whereas this is substantially reduced in the case of EDOT-OMeTPA. Note that the traces in (b) correspond to the results shown in the main text.

Figure S7: Magnification of the experimental (a) and modelled (b) TRMC traces for MAPbI₃/H101 as shown in Figure 5a of the main text.

Figure S8: Normalized TRMC traces for neat MAPbI₃ and bilayers of MAPbI₃/PCBM with different PCBM thickness (a) and trilayers of MAPbI₃/PCBM/C60, where C60 has a higher electron affinity than PCBM ($\lambda = 600$ nm, front side illuminated).

Figure S9: Photoluminescence emission scans (a) and lifetimes (b) for the neat MAPbI₃ and bilayer samples shown in the main text.