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Ultrafast Triplet Generation at the Lead Halide Perovskite/Rubrene Interface

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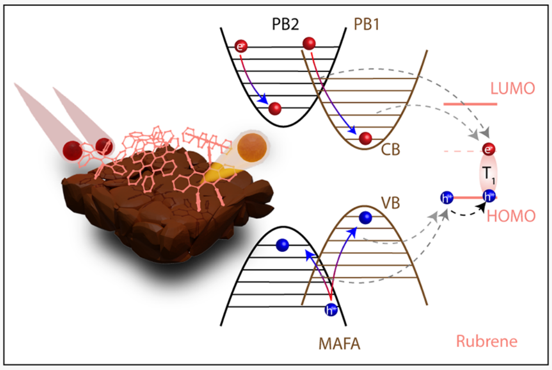
ABSTRACT: Triplet sensitization of rubrene by bulk lead halide perovskites has recently resulted in efficient infrared-to-visible photon upconversion via triplet−triplet annihilation. Notably, this process can occur under solar relevant fluxes, potentially paving the way toward integration with photovoltaic devices. In order to further improve the upconversion efficiency, the fundamental photophysical pathways at the perovskite/rubrene interface must be clearly understood to maximize charge extraction. Here, we utilize ultrafast transient absorption spectroscopy to elucidate the processes underlying triplet generation at the perovskite/rubrene interface. Our results point to a triplet generation mechanism based on hot carriers; thermally excited charge carriers in the perovskite cool more rapidly in the presence of rubrene, suggesting rapid extraction of these thermally excited carriers on the picosecond time scale. Subsequent triplet formation in rubrene is observed on a subnanosecond time scale.



Silicon-based solar cells, the current workhorse of solar energy, cannot absorb wavelengths beyond 1100 nm, limiting the efficient use of the entire solar spectrum.[1−3] A promising approach to overcome this fundamental limitation is the use of photon upconversion (UC).[4−9] Particularly promising is UC via triplet−triplet annihilation (TTA) in organic semiconductors, as it can become efficient at solar-relevant incident powers.[10−12] Due to spin selection rules, the spin-triplet states required for TTA-UC are populated via energy transfer from triplet sensitizers that generate triplet states through intersystem crossing,[8,13,14] inherently exhibit an excitonic wave function that possesses both triplet and singlet character,[7,15−18] or through asynchronous charge transfer (CT) processes from bulk lead halide perovskite materials.[12,19−25]

The long free carrier lifetimes, high absorption cross sections, and facile bandgap tunability of perovskites,[26−29] which are desirable properties in photovoltaic applications also yield the required foundation for triplet sensitization.[12,19−23] It is established that lead halide perovskites of varying halide and A-site compositions are capable of sensitizing the triplet state of rubrene. However, to date, the exact mechanism of triplet sensitization is still unclear.[30−33] Understanding the fundamental mechanism of triplet sensitization at the perovskite/organic interface will be the key in further improving perovskite-based UC, as it will unlock engineering pathways to further increase the device performance.

We have previously observed a lack of strong perovskite photoluminescence (PL) quenching in the presence of rubrene despite obvious upconversion occurring, which was attributed in part to strong back transfer of the upconverted singlets and surface passivation effects.[12,20,22] However, this observation may also indicate a more intricate triplet sensitization mechanism than the current simplistic view of direct charge carrier extraction from the perovskite to rubrene (Figure 1a). Particularly, it emphasizes that only a small fraction of free charges created upon photoexcitation are successfully extracted and return upconverted photons despite the long-lived nature of the free carriers in the perovskite, which should allow a large number of charges to be extracted within their lifetime.[23,28] Possible causes include localized states mediating electron and hole transfer and limiting the number of generated triplet states[30,31] and short-lived transient states (e.g., hot carriers) being involved in the triplet generation process.[34] In addition,

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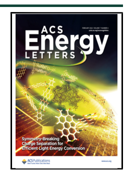

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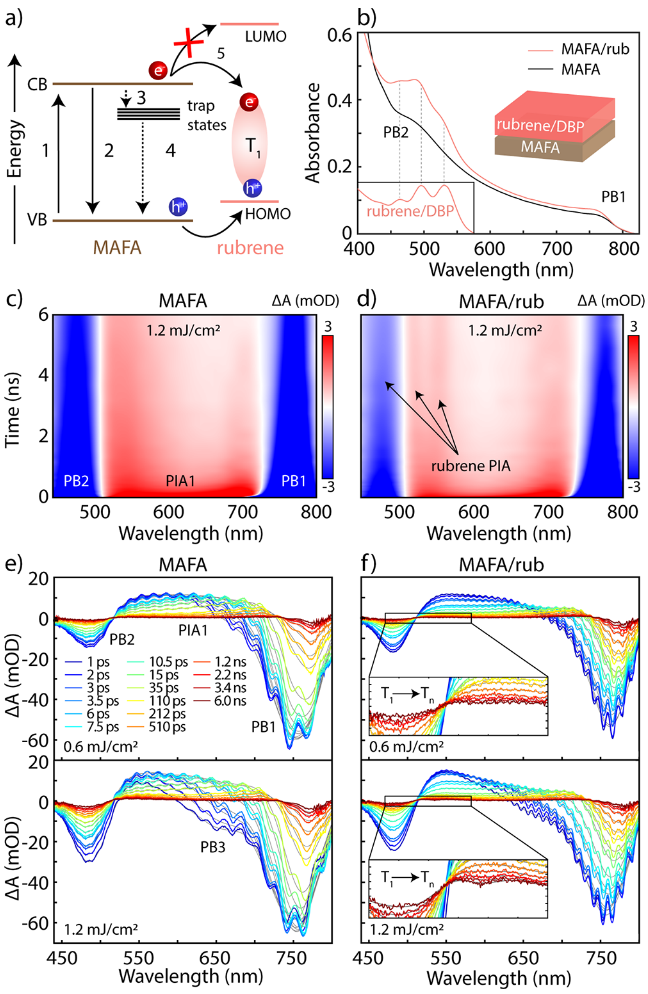

Figure 1. (a) Schematic of the current rubrene sensitization mechanism. (1) Photon absorption excites an electron from the VB to the CB. The excited state can relax to the ground state via (2) free carrier recombination, (3) charge trapping followed by (4) trap-assisted charge carrier recombination, or (5) charge transfer to the triplet state of rubrene. (b) Absorbance spectra of MAFA and MAFA/rub. The spectral regions of the two photobleaches observed in TA are labeled with PB1 and PB2. The insets shows the absorption spectra of a rubrene/DBP film and the device structure. (c) TA surface of MAFA and (d) MAFA/rub under 700 nm excitation at a pulse power of 1.2 mJ/cm^2. The two photobleaches are labeled with PB1 and PB2, the photoinduced absorption of MAFA is labeled PIA1. The rubrene PIAs are highlighted in (d). To remove the strong etalon feature, the TA surfaces were processed with a frequency filter. (e,f) Absorbance spectra at selected delay times for MAFA (e) and MAFA/rub (f) at 0.6 mJ/cm^2 (top) and 1.2 mJ/cm^2 (bottom) pulse power. The gray lines depict the frequency-filtered data. The additional photobleach observed at short delay times is denoted as PB3. The insets highlight the PIA corresponding to the $T_1 \rightarrow T_n$ transition of rubrene at 521 nm and polaron feature at 553 nm.

this simple mechanism does not consider the possible influence of midgap trap states or higher energy transitions in the perovskite which may also play a role in the triplet sensitization process.[35−37]

In this contribution, we utilize ultrafast transient absorption (TA) spectroscopy to investigate the photophysical processes occurring at the interface of $MA_{0.85}FA_{0.15}PbI_3$ (MAFA) and rubrene doped with ∼1% dibenzotetraphenylperiflanthene (DBP). The resulting bilayer UC devices are denoted as MAFA/rub in the following (inset Figure 1b). In Figure 1b, the steady-state absorption of the MAFA thin film and MAFA/rub bilayer is shown. The vibronic features of the rubrene/DBP absorption spectrum are highlighted, as well as the region of the two photobleaches (PB1, PB2) commonly observed in TA spectroscopy of lead halide perovskites.[34−36,38,39] The transient absorption data measured under 700 nm (pulse energy: 1.2 mJ/cm^2) excitation is plotted in Figure 1c,d as a temperature plot to allow the time-dependent evolution of the absorption features to be visualized. Figure 1e,f shows the extracted absorbance spectra for MAFA and MAFA/rub at different probe time delays under 700 nm excitation and pulse energies of 0.6 and 1.2 mJ/cm^2.

PB1 corresponds to the perovskite ground-state bleach at 780 nm, while the origin of PB2 at 485 nm in perovskites is still under debate; PB2 has been attributed to band filling effects stemming from two VBs and a shared CB,[36,39] one shared VB and two CBs,[38,39] or a high energy CT state, which is attributed to an I_2-like species formed under optical excitation.[35] In addition, a broad photoinduced absorption (PIA1) can be observed between 510 and 700 nm, which has been assigned to photoinduced refractive index changes or excited-state transitions stemming from free carriers.[34,40]

In the MAFA/rub device, additional overlapping PIAs are observed at ∼480, 520, and 550 nm (Figure 1d), which correspond to the rubrene triplet excited-state $T_1 \rightarrow T_n$ transitions and polaron signature, respectively (compare with Figure S1).[41−44] The excited-state triplet absorption signal in MAFA/rub confirms the successful rubrene triplet sensitization under 700 nm excitation. Comparing the TA surfaces of MAFA and MAFA/rub in Figure 1c,d and the extracted spectra in Figure 1e,f, we find no unexpected absorbing features in the presence of rubrene within the measurement window. In addition, no signature of a long-lived (e.g., defect-related) state within the spectral window of the measurement is found.

Further analysis of the TA data in Figure 1 reveals that PB2 (485 nm) exhibits distinctly different dynamics than PB1 (780 nm),[35] and both PB levels recover more rapidly in the presence of rubrene (vide infra). Similarly, PIA1 is reduced more rapidly. Therefore, the data indicate that the carriers populating the electronic states of this higher excited state may play a role in the UC process. It has been suggested that PB2 (485 nm) can be populated by direct absorption, a hot carrier/phonon-based mechanism, or an Auger-based population of the high energy state.[35,38] To determine if the population of PB2 (485 nm) influences the triplet generation process, we investigate the response of MAFA and MAFA/rub to different excitation wavelengths (compare with Figure S2 for 808 nm excitation) and different excitation powers.

The absorbance spectra of MAFA/rub for a wider range of pump energies (0.45−10.5 mJ/cm^2) at selected delay times of 1.5 ps, 100 ps, 1 ns, and 4 ns for MAFA/rub are shown in Figure 2, clearly showing the characteristic rubrene $T_1 \rightarrow T_n$ triplet excited-state PIA at a delay time of 4 ns, as well as the polaron signature at 553 nm. The relationship between the incident power and the bleach intensity of PB1, PB2, and PB3 at a delay time of 1.5 ps is shown in Figure S3. The power dependence of the PIA1 and overlapping rubrene-related PIA is found in Figure S4 for various delay times. With increasing power, we find an increase in the bleach intensity of all of the photobleaches, as well as an increase in the intensity of PIA1 and the rubrene $T_1 \rightarrow T_n$ and polaron PIAs.

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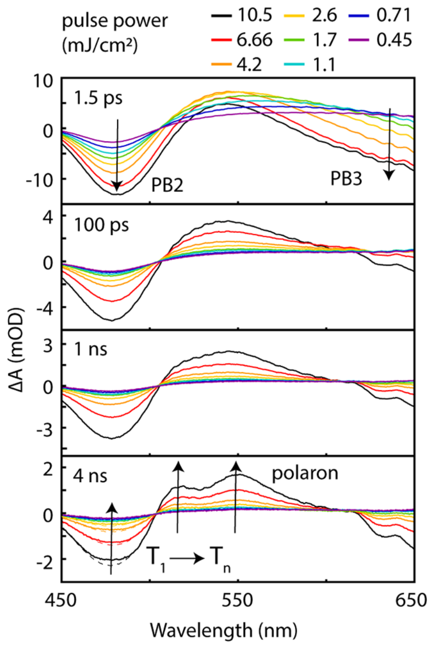

Figure 2. MAFA/rub absorbance spectra at excitation power densities ranging from 0.45 to 10.5 mJ/cm^2 obtained at delay times of 1.5 ps, 100 ps, 1 ns, and 4 ns under 700 nm excitation. The arrows are guides to the eye to highlight the increase in the PBs with increasing power and the growth of the rubrene triplet-related PIA $T_1 \rightarrow T_n$, as well as the polaron PIA. The dashed lines (bottom) are a guide to the eye to highlight the effect of the overlapping rubrene triplet PIA on PB2.

We have previously established that the power dependence of perovskite-sensitized TTA-UC is dependent on the underlying perovskite recombination dynamics and does not simply exhibit the characteristic quadratic-to-linear trend of TTA.[12] By extracting the triplet-related PIA from the residual underlying perovskite PIA1, we find a superlinear growth ($\alpha \approx 1.5$) of the triplet state based on incident power (Figure S4e,f). The observed nonlinear dependence of the triplet formation on the excitation power further confirms this observation and indicates that the triplet generation is not simply proportional to the number of incident photons.

To shed more light onto the underlying mechanism of triplet sensitization, we investigate the kinetics under 700 nm excitation (1.2 mJ/cm^2) at the MAFA ground-state bleach (PB1, 780 nm) and the related PIA1 (700 nm), as shown in Figure 3a. The dynamics of PB1 are well fit by a triexponential function with an offset (eq 1), which is required since PB1 does not fully recover within the measurement window:

$$\Delta A(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) + A_4 \tag{1}$$

The characteristic time constants are listed in Table 1 for MAFA and MAFA/rub. We find that in the first 20 ps PB1

Table 1. Amplitudes (A) and Decay Time Components (τ) for PB1 (780 nm)[a]

	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)	A_4
MAFA	0.37	46	0.28	185	0.30	1063	0.10
MAFA/Rub	0.49	8.9	0.27	165	0.27	999	0.09

[a] A_4 corresponds to an infinite time constant, as PB1 does not fully decay within our measurement window.

rapidly recovers in the presence of rubrene, indicating ultrafast charge extraction from the perovskite to rubrene. However, at later times, the dynamics slow and the underlying MAFA kinetics are recovered, indicating a reduction in the rate of charge extraction or a population of carriers that are unaffected by the addition of rubrene, which we have previously attributed to charges in the bulk of the perovskite that do not reach the interface prior to recombination.[19,23]

PIA1 (700 nm) grows in more rapidly for MAFA/rub than MAFA, initially recovers faster, and then appears to stagnate at later times. This is the result of multiple factors. First, the overlapping PB3 (650 nm) recovers more rapidly in the presence of rubrene (Figure S5). Second, PIA1 is correlated to PB1 (780 nm), and ultrafast charge extraction results in a faster initial recovery. Third, formation of rubrene polarons can result in a long-lived overlapping PIA, as charged rubrene species exhibit PIAs in the spectral region between 520−900

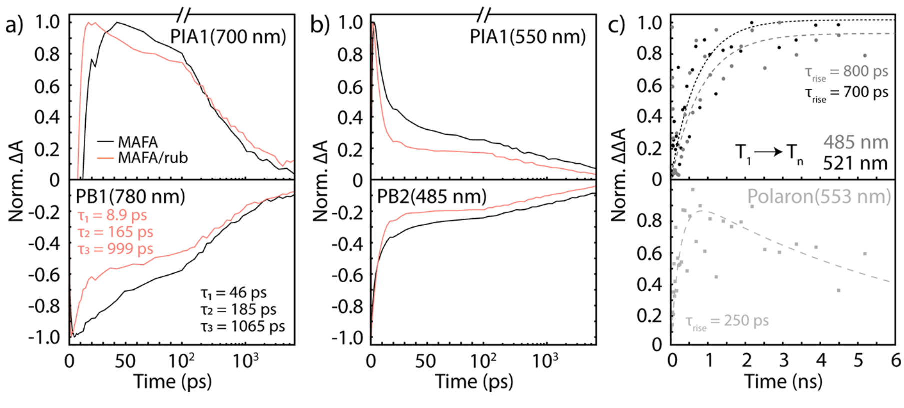

Figure 3. Normalized TA dynamics under 700 nm excitation at a power density of 1.2 mJ/cm^2 for MAFA (black) and MAFA/rub (pink). The dynamics were extracted at (a) 700 nm, PIA1 (top), 780 nm, PB1 (bottom) and (b) 550 nm, PIA1 (top), 485 nm, PB2 (bottom). (c) Normalized extracted kinetics for the overlaying rubrene $T_1 \rightarrow T_n$ transitions at 485 nm (gray) and 521 nm (black) and polaron PIA at 553 nm (light gray). We extract a rise time of τ_{rise} = 700 ps and τ_{rise} = 800 ps for the triplet $T_1 \rightarrow T_n$ transitions at 521 and 485 nm, respectively. The polaron has a characteristic rise time of τ_{rise} = 250 ps and begins to decay within the measurement window of 6 ns. The data were normalized to their maximum value.

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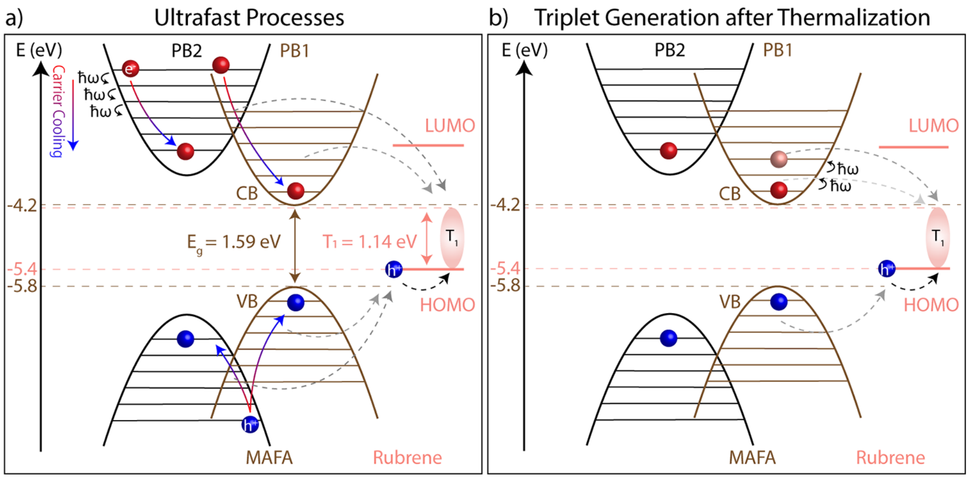

Figure 4. Proposed mechanism of triplet generation in MAFA/rub bilayer devices. (a) Optical excitation populates higher excited states. Hot carrier relaxation releases phonons ($\hbar\omega$) and the cooled carriers populate PB2 and the band edge PB1. Thermally excited carriers rapidly transfer to rubrene and combine to form the bound triplet state. (b) Once all carriers are thermalized and populate the band edges of PB1 and PB2, charge extraction to rubrene slows significantly, indicating the possible role of phonon-mediated transfer: phonons can excite carriers to higher excited states, from which charge extraction can occur efficiently.

nm,[45] which would effectively prolong the signal detected at this wavelength.

We also find a faster recovery of both PB2 (485 nm) and PIA1 (550 nm) in the presence of rubrene (Figure 3b), indicating this higher energy state is also influenced by the presence of rubrene. However, we cannot conclusively determine whether the state is directly quenched or the quenching is a result of an equilibrium with PB1 (780 nm), which is rapidly depopulated by the presence of rubrene. Yet, as evidenced by our power-dependent TA (Figures S3 and S4), a clear correlation exists between the initial population of this state and a high yield of triplet generation, which indicates that the same charge carriers which populate PB2 also generate the triplet state of rubrene.

To determine the rate of triplet generation, we take a closer look at the recombination dynamics of PB2 (485 nm) and PIA1 in the spectral region between 510 and 555 nm, as the triplet PIA is overlapping in this region (see Supporting Information for details and Figure S6). The resulting extracted triplet kinetics are well fit by a rise time of τ_{rise} = 700 ps for the $T_1 \rightarrow T_n$ transition at 521 nm and τ_{rise} = 800 ps for the $T_1 \rightarrow T_n$ transition at 485 nm (Figure 3c, top) and further highlight the expected persistence of the triplets beyond our measurement window. The polaron-related PIA at 550 nm is similarly fit with a rise time of τ_{rise} = 250 ps (Figure 3c, bottom) and begins to decay within our measurement window. We attribute this to triplet formation through the polaron state,[43,46] which is further supported by the increased intensity of the rubrene polaron feature relative to the $T_1 \rightarrow T_n$ transition in MAFA/rub than in the rubrene thin film (Figure S1b) and the decay of the polaron state within our measurement window.

To summarize thus far, we have established the following: (i) At higher excitation fluences and therefore higher effective carrier densities, an additional short-lived broad bleach signature (PB3, 650 nm) can be observed which rapidly decays as PB1 (780 nm) is populated. In agreement with previous work, we attribute this absorbing species to thermally excited (hot) carriers rapidly cooling to the lower energy band edge.[40,47−50] PB3 (650 nm) is more pronounced in MAFA than in MAFA/rub, indicating that the interaction between rubrene and the perovskite surface reduces the presence of this absorbing species, suggesting that hot charge carriers are directly extracted to rubrene (Figure 1e,f).[34] (ii) The intensity of PIA1 is more rapidly reduced in the presence of rubrene (Figure 3). We find PIA1 to initially red shift rapidly, which has been previously attributed to bandgap renormalization.[51] Up to ~200 ps, the spectral shape continues to evolve due to Auger relaxation,[39,52] after which PIA1 converges to a uniform spectral shape, with a clear isosbestic point at 730 nm (Figure 1f). (iii) PB2 (485 nm) is populated prior to PB1 (780 nm) (Figure 3) and both states can be accessed even under excitation at 808 nm (Figure S2), which is slightly below the optical bandgap of MAFA. This indicates the involvement of shallow traps and phonon-mediated excitation of both PB1 and PB2.[33] (iv) For both MAFA and MAFA/rub, PB1 (780 nm) is narrower at lower pulse power (Figure 1), further highlighting the effect of hot carriers on the TA spectra (vide infra). (v) The emergence of the rubrene triplet-related PIA is fluence dependent. Interestingly, we find a superlinear relationship between the triplet signal and the incident power (Figure S4), indicating more than one photon is required to generate one triplet state. (vi) No PbI_2-related signature is found (Figure S7), ruling out the role of PbI_2 as a mediating factor for triplet sensitization.

The proposed excited-state steps involved in the triplet generation in MAFA/rub are summarized in Figure 4, where the more rapid recovery of PB1 (780 nm) is attributed to charge extraction to rubrene. PB2 (485 nm) and the related PIA1 (550 nm) also exhibit accelerated recovery kinetics, indicating that this higher energy transition in the perovskite also plays a role in the triplet sensitization mechanism. Specifically, we propose that the thermally excited carriers that populate PB2 (485 nm) are extracted to rubrene and form the bound triplet state. The additional PB3 (650 nm) observed in MAFA is reduced in MAFA/rub, further emphasizing a change in the hot carrier properties upon addition of the organic molecules.

Our results, therefore, suggest that PB2 (485 nm) and PB3 (650 nm) are populated by a hot-carrier-based mechanism, and carrier extraction from MAFA to rubrene occurs rapidly

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while the charge carriers are thermally excited. Upon photoexcitation, hot carriers are generated which rapidly thermalize via elastic carrier−carrier scattering. Once equilibrated, hot carriers occupy states according to a Fermi−Dirac distribution with a dynamic quasi-Fermi level.[40,47,48] These hot carriers initially populate the higher excited states PB2 (485 nm) and PB3 (780 nm), from which they can either be extracted directly to the rubrene polaron or triplet state or act as a reservoir to repopulate PB1. Thermally excited charge carriers are directly extracted to rubrene and recombine to the bound triplet state (Figure 4a), as evidenced by the more rapid recovery of PB1 (780 nm) at early times, the increased carrier cooling (vide infra), and the emergence of the rubrene polaron and triplet-related PIA. Once the carriers have thermalized to the band edge, charge transfer to the rubrene triplet state slows down significantly, as the energetic driving force is reduced and subsequent charge transfer may require additional phonon support (Figure 4b).

Hot carriers would lead to a similar effect as previously observed in mixed halide systems, where the addition of bromide deepens the VB and moves the CB to a shallower level. This shift in the energetic alignment at the perovskite/rubrene interface effectively increased the yield of charge extraction in these mixed halide systems due to an increase in driving force for charge extraction.[33]

To support our proposed mechanism and investigate the properties of the hot carriers more fully, we track the carrier temperatures extracted from the TA spectra at different delay times (Figure 5a) and the shift of the quasi-Fermi level (E_F) over time (Figure 5b) under different excitation fluences at 700 nm.[48,51] In agreement with previous reports, we find higher carrier temperatures at higher pump fluences and that the hot-phonon bottleneck effect observed in perovskite thin films extends the carrier cooling time.[51,53] As expected for hot carrier extraction, in the presence of rubrene, the carrier temperatures for MAFA/rub cool at a faster rate than for MAFA. This is further highlighted by a lower quasi-Fermi level and a redder initial PB1 position for MAFA/rub than MAFA (Figure 5b,c). The effect of the different carrier temperatures can also be observed in the PB1 dynamics. We find that PB1 builds up more rapidly in the presence of rubrene and at lower excitation powers (Figure 5d), in agreement with previous reports on higher carrier temperatures resulting in a slower buildup of the ground-state bleach.[34] For an average pulse energy of 1.2 mJ/cm^2 (0.6 mJ/cm^2) at a pump wavelength of 700 nm, the time constant of the PB1 buildup of MAFA is 1.1 ps (0.5 ps) and shortens to 0.4 ps (0.3 ps) for MAFA/rub.

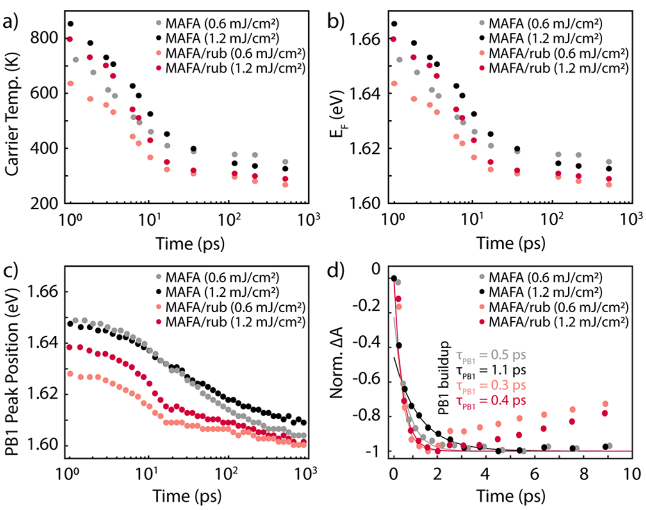

Figure 5. (a) Carrier temperatures under 700 nm excitation at various delay times and pulse powers for MAFA (black, 1.2 mJ/cm^2; gray, 0.6 mJ/cm^2) and MAFA/rub (magenta, 1.2 mJ/cm^2; pink, 0.6 mJ/cm^2). (b) The position of the quasi-Fermi level (E_f) as a function of the delay time for MAFA and MAFA/rub at pulse powers of 0.6 mJ/cm^2 (gray, pink) and 1.2 mJ/cm^2 (black, magenta). (c) Corresponding perovskite ground-state bleach (PB1) position as a function of time. (d) Normalized TA kinetics of MAFA (black, gray) and MAFA/rub (magenta, pink) under 700 nm excitation at pulse powers of 0.6 and 1.2 mJ/cm^2, extracted at PB1 (780 nm). The bleach is fit (solid line) with an exponential decay function, yielding the time constants shown as the PB1 buildup time. The kinetics were normalized to their maximum value.

In summary, we have investigated the MAFA/rubrene interface by means of ultrafast TA spectroscopy. Our results indicate ultrafast charge extraction and subsequent triplet generation on a subnanosecond time scale. The PIA at 550 nm has previously been attributed to polarons in rubrene and is generated at a faster rate than the triplet PIA (485 nm, 520 nm). The nonlinear response of the triplet generation indicates that the triplet generation does not rely on a simple "one photon in, one triplet out" mechanism. Rather, it is indicative of the involvement of higher order processes such as nongeminate free carrier recombination or Auger recombination. No spectroscopic signature of a localized CT state or long-lived trap states is found.

Therefore, in agreement with our previous results,[22,32,33] we emphasize that the key factor for triplet generation is the energetic alignment for charge injection from the VB and CB of the perovskite into the triplet state of rubrene. As shown in Figure 2, our results indicate that a strong population of PB2 (485 nm) and PB3 (650 nm) yields a strong triplet signature. Hence we propose that the same mechanism that populates PB2/PB3 also populates the triplet state, which we attribute to hot carriers.

A hot-carrier-based mechanism is further supported by our previous observation that the perovskite emission is not necessarily strongly quenched in the presence of rubrene: only carriers reaching the interface while they are "hot" can be efficiently extracted to the triplet state. Despite the long free carrier lifetime of halide perovskites, carriers generated further from the interface would cool prior to reaching the interface, limiting the number of carriers that can be extracted on an ultrafast time scale. However, at later times outside of our observation window, additional carriers are expected to more slowly transfer by taking advantage of the rich phonon bath present in perovskite materials as evidenced by the observed quenching of the photoluminescence decay dynamics on a nanosecond time scale.[22,33]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c02732.

Details of experimental methods, carrier temperature calculations, data analysis methods, and additional TA data (PDF)

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Author Contributions

[#]C.R.C. and A.S.B. contributed equally.

Notes

The authors declare the following competing financial interest(s): FSU has filed a provisional application for a US patent based on this technology that names L.N. and S.W. as inventors.

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