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LETTER

The Potential of Singlet Fission Photon Multipliers as an Alternative to Silicon-Based Tandem Solar Cells

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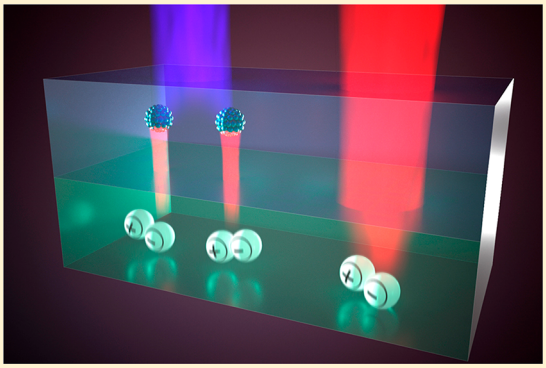
Supporting Information

ABSTRACT: Singlet fission, an exciton multiplication process in organic semiconductors that converts one singlet exciton into two triplet excitons, is a promising way to reduce thermalization losses in conventional solar cells. One way to harvest triplet excitons is to transfer their energy into quantum dots, which then emit photons into an underlying solar cell. We simulate the performance potential of such a singlet fission photon multiplier combined with a silicon base cell and compare it to a silicon-based tandem solar cell. We calculate the influence of various loss mechanisms on the performance potential under real-world operation conditions using a variety of silicon base cells with different efficiencies. We find that the photon multiplier is more stable against changes in the solar spectrum than two-terminal tandem solar cells. We furthermore find that, as the efficiency of the silicon base cell increases, the efficiency of the photon multiplier increases at a rate higher than that of the tandem solar cell. For current record silicon solar cells, the photon multiplier has the potential to increase the efficiency by up to 4.2% absolute.



Crystalline silicon solar cells dominate the global solar cell market, and record efficiencies of 26.7% approach the Auger-recombination-constrained Shockley−Queisser limit.[1−3] For further improvement in the power-conversion efficiency new solutions beyond the silicon single-junction cell are needed.

Conventional solar cells lose a major part of incident sunlight energy via thermalization of excited charge carriers.[4] For a silicon solar cell with a band gap of 1.12 eV, thermalization accounts for a 39% power loss using the AM1.5G solar spectrum. The reduction of thermalization losses thus offers a great opportunity to achieve efficiencies above the Shockley−Queisser limit. Many strategies have been proposed to reduce thermalization losses of silicon solar cells, including tandem configurations and the modulation of the solar spectrum by down conversion.

In a tandem configuration with two subcells, a high-band-gap cell is placed on top of a low-band-gap cell.[5] Photons with a high energy are absorbed in the top cell, and the transmitted light is absorbed in the bottom cell, reaching record efficiencies of 32.8% with III−V semiconductors as the top cell and silicon as the bottom cell in a four-terminal configuration.[6] Perovskites are a class of materials that promise cost-effective and efficient tandem solar cells in combination with silicon.[7−9] However, tandem solar cells add extra costs and complexity to the fabrication process. They are furthermore sensitive to changes in solar spectrum and temperature during the course of a year, which reduces their efficiency under real-world conditions compared to laboratory conditions.[10,11]

While tandem solar cells are studied extensively, partially because of the recent boom in perovskite research, alternatives such as spectral modulation have received considerably less attention. Modulating the solar spectrum by either up- or down-conversion of photons,[12−18] single-junction solar cells can operate at an efficiency comparable to that of tandem solar cells.[13] A down-conversion device absorbs high-energy photons with at least twice the band gap energy and emits twice as many photons with about half that energy. We call this device a "photon multiplier".

Singlet fission, a spin-allowed exciton multiplication process in organic semiconductors which converts one singlet exciton into two triplet excitons,[19] is a suitable process for such a photon multiplier. Upon photoexcitation, organic semiconductors generate singlet excitons. If the energy of these singlet excitons $E(S_1)$ is close to twice the energy of the lowest-lying triplet

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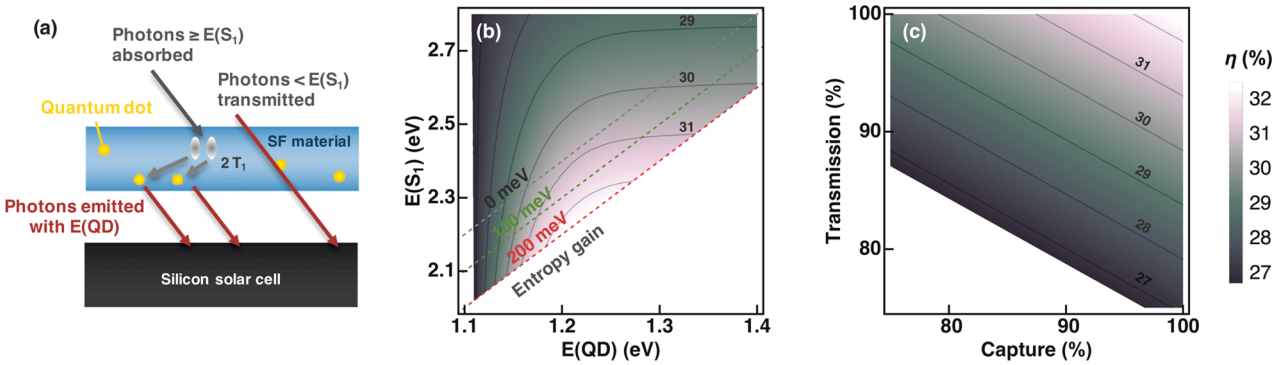

Figure 1. (a) Schematic illustration of the singlet fission photon multiplier device. (b) Efficiency of the singlet fission photon multiplier as a function of singlet exciton energy $E(S_1)$ and energy of quantum dot emission $E(QD)$ assuming no transmission and capture losses. (c) Efficiency of the singlet fission photon multiplier as a function of capture and transmission losses below $E(S_1)$. The capture parameter is defined in the text as $\eta_{SF}/2 \times \eta_T \times \eta_{QD} \times \eta_C$. The calculations are performed at standard test conditions using a silicon base cell with an efficiency of 26.7%.

exciton $E(T_1)$, i.e. $E(S_1) \approx 2E(T_1)$, singlet fission ($S_1 \rightarrow 2T_1$) can occur on sub-100 fs time scales.[20] Singlet fission has been observed with very high efficiency,[21−24] even for endothermic singlet fission, i.e. $E(S_1) < 2E(T_1)$. We note that there likely is an inevitable trade-off between entropic gain and triplet exciton yield. However, endothermic singlet fission with barriers as high as 200 meV was shown to be still highly efficient.[25] Triplet excitons can then transfer their energy to an inorganic semiconductor directly via a charge or an energy transfer or via a quantum-dot-mediated intermediate state.[26] While direct energy transfer into silicon would be desirable, as it avoids all other loss channels, it has not been shown to date[27] and would require changes to the silicon solar cell architecture. In contrast, the photon multiplier is a purely optical downconverter, which allows for easy integration into existing solar cell technologies without the need for changes to the underlying solar cell, even as an upgrade (see Figure 1a). To form the photon multiplier, the triplet excitons first transfer their energy into quantum dots (QDs). Within the QDs, the excitons recombine to emit photons,[28,29] whereby the exciton multiplication process becomes a photon multiplication process. Further details on singlet fission and the photon multiplier concept can be found in a recent review.[30]

The efficiency limit of singlet fission solar cells essentially matches the efficiency limit for a two-junction tandem solar cell.[31] However, these efficiency limits are calculated for ideal cells under standard test conditions, and both cell types have very different potential loss mechanisms and a very different dependence on environmental conditions. Hence, here we simulate the potential performance of both types, but with realistic electrical and optical parameters, and simulate them under real-world environmental conditions using a variety of silicon base cells with different efficiencies. We simulate the performance of the current-matched series, the voltage-matched module, and the electrically independent four-terminal perovskite/silicon tandem solar cell. In the analysis, however, we focus on the series tandem, as the monolithic two-terminal configuration is the most attractive from an industrial point of view.[32] Our simulations provide clear guidelines to optimize photon multiplier devices by including physical parameters such as the energy of the singlet exciton, the energy and the full width at half-maximum (fwhm) of the QD emission, losses due to absorption, transfer efficiency, and imperfect guiding of the emitted photons toward the bottom cell. We find that the photon multiplier is more stable against changing irradiation, spectral shape, and temperature than tandem solar cells, which are important factors in real-world performance. We furthermore find that, as the efficiency of the silicon base cell increases, the photon multiplier gains faster in efficiency than the tandem solar cell and that for current record silicon solar cells, the photon multiplier has the potential to increase the efficiency by up to 4.2% absolute.

To simulate the performance of the singlet fission photon multiplier in combination with a silicon solar cell, we model the modulation of the solar spectrum. The efficiency of the silicon solar cell is then calculated using our previously developed method and the modulated solar spectrum.[10] The silicon solar cell is modeled by including realistic solar cell parameters such as Auger recombination, nonradiative recombination, and parasitic series and shunt resistance into detailed-balance calculations. To include parasitic absorption of the contacts, we include the external quantum efficiency (EQE) in the model. This allows for simulating the performance of both the silicon solar cell and the photon multiplier for changing solar spectra and temperatures (see section S1 in the Supporting Information for details).

For a photon multiplier that absorbs all light above the energy of the singlet exciton $E(S_1)$ and where the QDs emit at the energy $E(QD) = 1/2\ E(S_1)$ with a fwhm of 30 meV, the optimum energetics are $E(QD) = 1.21$ eV and $E(S_1) = 2.42$ eV. Including entropic gain, the optimal singlet exciton energy shifts to lower energies, while the energy for QD emission remains almost constant. At 200 meV entropic gain, the optimum would be at $E(QD) = 1.22$ eV and $E(S_1) = 2.24$ eV, where the efficiency of the record silicon solar cell would be enhanced from 26.7% to 32.5% (see Figure 1b).

In the following, we discuss the losses which for real devices will reduce this efficiency potential. To take transmission losses due to parasitic absorption and reflection by the photon multiplier into account, we assume that photons with an energy below $E(S_1)$ are homogeneously absorbed or reflected before reaching the silicon solar cell. Using transfer matrix simulations, we show that the reflection above the singlet fission band gap is less than 7% when placing a photon multiplier on top (see section S2 in the Supporting Information for details). This value is likely to be improved by texturing and antireflection optimization. In addition, we consider losses during the photon multiplication process, which are collectively referred

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to as capture losses. The efficiency of the singlet fission photon multiplier for different combinations of absorption and capture losses assuming a 30 meV fwhm for the QD emission and 200 meV entropic gain is shown in Figure 1c. These capture losses include the triplet exciton yield from singlet fission (η_{SF}), the efficiency of triplet excitons diffusing to and transferring into the QDs (η_T), the photoluminescence quantum efficiency (PLQE) of the QDs (η_{QD}), and the fraction of photons emitted by the QDs toward the silicon solar cell (η_C). In the following we compare two cases of photon multipliers. A realistic case with an efficiency of 29.0% and an optimistic case with an efficiency of 31.3% using the record silicon base cell with an efficiency of 26.7% (for parameters, see Table 1). In the realistic and optimistic cases we assume a capture of 85% and 95%, respectively, which assumes high values for η_{SF}, η_T, η_{QD}, and η_C. In the following we provide evidence that these are, however, not unreasonable.

Table 1. Parameters and Performance of the Realistic and the Optimistic Singlet Fission Photomultiplier Calculated at Standard Test Conditions Using a Silicon Base Cell with an Efficiency of 26.7%[a]

	entropic gain (meV)	transmission (%)	capture (%)	fwhm (meV)	η (%)
realistic case	100	95	85	30	29.0
optimistic case	200	97	95	30	31.3

[a]The capture parameter is defined in the text as $\eta_{SF}/2 \times \eta_T \times \eta_{QD} \times \eta_C$.

The triplet exciton yield from singlet fission (η_{SF}) was shown to reach values close to 200% for pentacene-based devices.[21−24] Because triplet transport occurs through a Dexter mechanism, triplets diffuse much slower than singlet excitons.[33] For endothermic singlet fission, however, triplet diffusion is enhanced by singlet-mediated pathway that allows for long diffusion lengths of triplet excitons.[34,35] The energy transfer from the triplet exciton to the QDs via Dexter transfer (η_T) has been demonstrated with efficiencies >95% for lead chalcogenides-based QDs.[28,29] We note that singlet excitons can also transfer their energy to the QDs; this is, however, negligible for SF materials with fast dynamics, because fission should kinetically out-compete energy transfer into the QDs. Because of the long triplet exciton diffusion length,[34−36] only a small number of QDs need to be embedded in the singlet fission material. Ideally, the QDs are distributed evenly throughout the singlet fission material, spaced by the triplet diffusion length. We estimate that QDs distributed in a micrometer-thick singlet fission layer, spaced by 50 nm, would absorb less than 0.5% of the transmitted light and therefore do not consider any reabsorption losses in our model (see section S2 in the Supporting Information for details). Although the highest reported PLQE for lead chalcogenides-based QDs (η_{QD}) with the desired energy of emission is only close to 50%,[37,38] we expect a PLQE of >95% to be realistic in the future, because QDs optimized for PLQE (e.g., metal chalcogenide and pnictide core−shell and lead halide perovskite QDs)[39] reach PLQE values close to unity. Part of the isotropic QD emission falls within the escape cone determined by the critical angle and is lost. For a SF material with a refractive index of 1.7, already less than 10% of light is within the escape cone (see section S2 in the Supporting Information). The other part is directly emitted into, or guided by total internal reflection toward the silicon bottom cell. The fraction of light guided to the silicon base cell (η_C) can further be increased by using a SF material with a high dielectric constant or by asymmetric dielectric nanostructures close to the quantum dot emitters.

The current−voltage characteristics of the modeled realistic and optimistic photon multiplier together with the modulated photon flux reaching the silicon solar cell filtered by its EQE are shown in Figure 2a. The effect of fwhm on the efficiency is relatively small; however, a wider emission spectrum does shift the ideal QD band gap to slightly higher energies (Figure 2b; see also the Supporting Information).

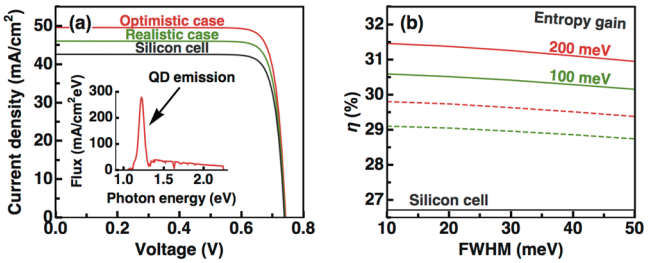

Figure 2. (a) Current−voltage characteristics of the modeled singlet fission photon multiplier on the silicon base cell with an efficiency of 26.7% for the optimistic case and the realistic case. The inset shows the modulated photon flux incident on the silicon base cell filtered by its external quantum efficiency. (b) Efficiency of the singlet fission photon multiplier as a function of full width at half-maximum (fwhm) for the quantum dot emission using a silicon base cell with an efficiency of 26.7%. The solid (dashed) lines assume 3% (5%) parasitic absorption losses below the singlet fission band gap and capture losses of 5% (15%). The black solid line indicates the efficiency of the silicon solar cell.

To compare the potential of the photon multiplier to tandem solar cells, we simulate a monolithic two-terminal perovskite/silicon tandem solar cell with all parameters based on the record perovskite solar cell with an efficiency of 22.7% and an area of 0.09 cm^2,[40] except that we change the band gap to the ideal value of 1.68 eV in order to current-match the perovskite top cell with the silicon bottom cell. The record perovskite cell features a shunt resistance of 5000 Ω cm^2, a series resistance of 0.32 Ω cm^2, and an electroluminescent emission efficiency of 0.15%. This leads to an efficiency of 20.9% for the perovskite solar cell and 32.7% for the tandem solar cell in combination with the record silicon solar cell with an efficiency of 26.7% (see section S3 in the Supporting Information for details). We note that we did not include any possible optical or electrical losses from the intermediate recombination layer required in practical tandem cells. The performance characteristics of the perovskite cell assumed here are hence optimistic and have not yet been achieved with this band gap.

To simulate real-world conditions, we use solar spectra, irradiance, and temperatures measured in Utrecht, The Netherlands and in Denver, Colorado (US) in 2015 at an interval of 30 min during daylight hours,[41,42] as described in previous work.[10]

Figure 3a shows that the efficiency of the tandem solar cell and the photon multipliers over the course of the year. Because the photon multiplier acts as a passive optical film modulating the incident solar spectrum, no electrical contact with the silicon solar cell is required. The photon multiplier thus shifts the silicon solar cell to higher efficiencies without considerably changing its dependence on the irradiance. The difference to the tandem cell is most prominent in the low-intensity region.

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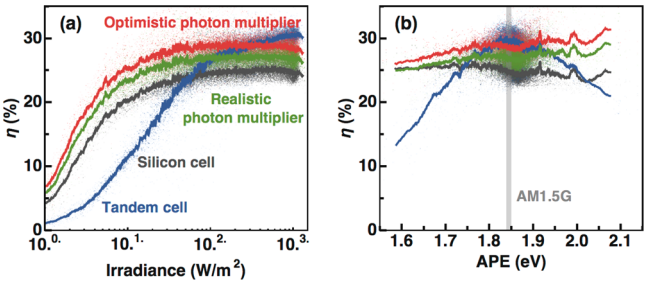

Figure 3. Efficiency of the two singlet fission photon multipliers, the tandem solar cell, and the silicon solar cell as a function of (a) irradiance and (b) average photon energy (APE) using solar spectra and temperatures measured in The Netherlands and in Colorado with the record silicon base cell with an efficiency of 26.7%.[41,42] The solid lines represent the moving average of the data. The APE is calculated for photons with an energy above the band gap of silicon. The gray line indicates the APE of the AM1.5G standard solar spectrum.

The decrease in efficiency for tandem cells at low irradiance is due to the shunt resistance from the perovskite top cell that adds to the shunt resistance from the silicon cell alone. At high irradiances, the tandem solar cell overtakes the silicon solar cell and the two photon multipliers, as the increased shunt resistance at high current density is relatively less important.

Figure 3b shows that the efficiency of the silicon solar cell is only weakly affected by spectral changes, while the photon multiplier improves in efficiency with increasing average photon energy (APE). This is due to the modulation of the solar spectrum by the photon multiplier, which makes better use of the blue part of the incident solar spectrum. The tandem cell on the other hand is strongly affected by a shift of the APE away from standard test conditions because of the current-matching constraint of the monolithic two-terminal configuration. In a monolithic two-terminal configuration, the generated current is limited by the cell producing the lower current. A change in the spectral irradiance distribution therefore leads to a discrepancy between the current generated in the two subcells, which reduces the efficiency of the tandem solar cell. We note that we used values only with an irradiance greater than 50 W/m^2 in Figure 3b to highlight the effect of APE on the efficiency, which would otherwise be skewed by the reduction in efficiency of the various cells at low intensity. Figure S6 shows the APE including all irradiances.

In addition to the record silicon solar cell, we simulate the performance of the two photon multipliers and the tandem solar cell using a variety of silicon base cells with (certified) efficiencies varying from 17.8% to 26.7% under standard test conditions. We also include two silicon solar cells with no nonradiative recombination, with unity EQE, and with Auger recombination (29.9%) and without (30.6%). The band gap of the perovskite solar cell, $E(S_1)$, and $E(QD)$ were optimized for each silicon solar cell (see section S4 in the Supporting Information for details). Figure 4a shows the efficiencies of the tandem cell and the silicon cells with a photon multiplier, as a function of the silicon base cell efficiency under standard test conditions. The photon multiplier increases the current of the silicon solar cells by an almost constant percentage without changing the electrical properties. As a result, the absolute efficiency increase by the photon multiplier is almost constant for all silicon cells and even increases slightly for more efficient silicon cells (the slope is 1.1 in Figure 4a for the realistic case and 1.3 for the optimistic case). That increase is due to the (on average) higher EQE of the efficient silicon cells close to the band-edge which allows for more efficient use of the photons emitted from the photon multiplier. In addition, the QD emission is slightly shifted toward the red for cells with a high EQE near the band edge, allowing for higher current gain.

In contrast, the tandem cell improves less upon the silicon cell efficiency for higher silicon efficiencies with a slope of 0.5 in Figure 4a. This arises because the perovskite front cell shades part of the spectrum reaching the cell underneath, which leads to a larger loss for an efficient silicon base cell. The difference in efficiency between the tandem cell and the photon multiplier thus becomes lower the more efficient the silicon base cell becomes, and the photon multiplier becomes as efficient as the tandem cell at a silicon base cell efficiency of 28.2% for the optimistic and 32.0% for the realistic case under standard test conditions.

Under realistic conditions, the slopes of the efficiency of the tandem cell and the photon multipliers against the silicon base cells remain roughly constant (see section S4 in the Supporting Information for linear fit parameters of Figure 4). However, the tandem cells show higher losses than the silicon cell alone compared to standard test conditions (offset of the fit in Figure 4), while the photon multiplier follows the efficiency drop of the silicon solar cell (see Figure 4b,c). This was already evident from Figure 3, because the dependence on irradiance and APE match the dependence of the silicon cell. The efficiency of the photon multiplier is therefore rather insensitive to the location of deployment, as is the efficiency of the silicon cell. In contrast, the efficiency of the tandem solar cell is strongly

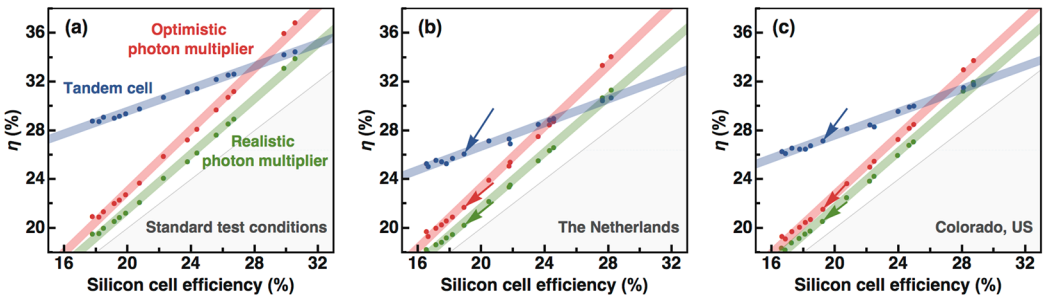

Figure 4. Efficiency of the two singlet fission photon multipliers and the tandem solar cell as a function of the silicon base cell efficiency under (a) standard test conditions and under real-world conditions averaged over the entire year and weighted with the incoming intensity, calculated using solar spectra and temperatures measured in (b) The Netherlands and (c) Colorado.[41,42] The arrows indicate the change in efficiency from standard test conditions to real-world conditions.

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dependent on the location of deployment because of its sensitivity to changes in the solar spectrum. As a result, the efficiency of the tandem cell in The Netherlands is lower than that in Colorado. We note that the voltage-matched module tandem and the electrically independent four-terminal tandem are somewhat less sensitive to changes in the solar spectrum than the current-matched series tandem. However, the slope of the tandem efficiency against the efficiency of the silicon base cell is 0.5 for all three different tandem configurations (see section S6 in the Supporting Information for details). The average intensity-weighted efficiency reduction due to real-world conditions is 2% for the two photon multipliers and the silicon solar cell in The Netherlands and in Colorado, while the efficiency of the series tandem cell is reduced by 3% in Colorado and by 4% in The Netherlands. The photon multiplier will then already be as efficient as the tandem solar cell at a silicon base-cell efficiency of 24.4% (26.6%) for the optimistic and 27.7% (28.9%) for the realistic case in The Netherlands (Colorado).

In conclusion, we simulate the performance potential of a singlet fission photon multiplier in comparison to a two-terminal tandem solar cell under real-world operation conditions. Compared to tandem solar cells, the photon multiplier has the advantage that it can be easily integrated into existing solar cell technologies, without the need for electrical contacts with the underlying solar cell. Unlike monolithic two-terminal tandem cells, the photon multiplier does not require current matching, making it more stable against changes in the solar spectrum.

To improve the efficiency of silicon solar cells by modulating the incident solar spectrum, however, some requirements must be met. The singlet fission material must have a high triplet exciton yield and a strong absorption. Furthermore, efficient energy transfer of the triplet excitons into the QDs is necessary, which must emit between 1.2 and 1.3 eV with a high PLQE. A large proportion of the emitted photons must then be directed toward the underlying silicon solar cell. If this is achieved, we find that a photon multiplier can increase the efficiency of the record silicon solar cell by up to 4.2% absolute even at real-world environmental conditions, with little dependence on the location of deployment. The purely optical method of modulating the incident solar spectrum with a singlet fission photon multiplier thus offers a promising way to reduce thermalization losses.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b01322.

> Additional information on the singlet fission photon multiplier model, the perovskite/silicon tandem solar cell model, the modeled silicon solar cells, and additional tandem configurations (PDF)

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Notes

The authors declare no competing financial interest.

Simulations of the solar cell efficiencies are performed using Mathematica. The code can be downloaded free of charge at https://github.com/HybridSolarCells.

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