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A Silicon−Singlet Fission Tandem Solar Cell Exceeding 100% External Quantum Efficiency with High Spectral Stability

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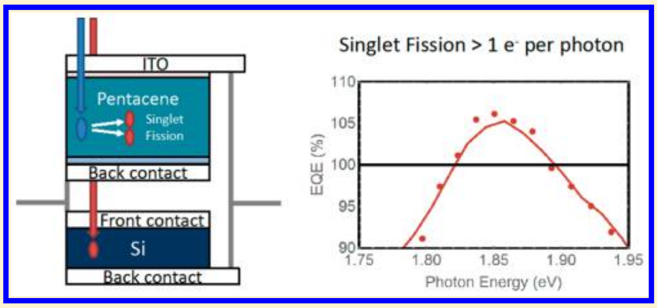
Supporting Information

ABSTRACT: **After 60 years of research, silicon solar cell efficiency saturated close to the theoretical limit, and radically new approaches are needed to further improve the efficiency. The use of tandem systems raises this theoretical power conversion efficiency limit from 34% to 45%. We present the advantageous spectral stability of using voltage-matched tandem solar cells with respect to their traditional series-connected counterparts and experimentally demonstrate how singlet fission can be used to produce simple voltage-matched tandems. Our singlet fission silicon−pentacene tandem solar cell shows efficient photocurrent addition. This allows the tandem system to benefit from carrier multiplication and to produce an external quantum efficiency exceeding 100% at the main absorption peak of pentacene.**



Conventional single-junction solar cells are limited in efficiency to about 34%, mainly because of non-absorbed below-band-gap photons and the loss of energy via thermalization of high-energy electron−hole pairs. This limit is called the Shockley−Queisser limit.[1] Singlet fission is a down-conversion process in organic semiconductors that spontaneously converts one high-energy spin-singlet electron−hole pair (exciton) into two spin-triplet excitons.[2] Each triplet exciton carries half the energy of the initial singlet exciton. Utilized in solar cells, this process could lift the theoretical limit of a single junction[3,4] when combined with a lower-band-gap semiconductor.

In previous work, we and others have shown successful examples which incorporated pentacene as the singlet fission sensitizer for lead chalcogenide quantum dots[5−7] or amorphous silicon.[8] Here we use a novel architecture, combining a conventional monocrystalline silicon solar cell with a pentacene cell connected electrically in parallel. In such a parallel tandem architecture, the efficiency of silicon photovoltaics can be enhanced with singlet fission by potentially doubling the current obtained from high-energy photons. Tandem solar cells already overcome[9] the single-junction Shockley−Queisser limit by stacking two or more solar cells with a different band gap in series such that light passes the high-band-gap material before it reaches the lower-band-gap subcell(s) (see Figure 1A). In this configuration, steady-state is reached when the voltages of the subcells add, and the currents match. A mismatch between the current generated by each subcell forces a shift on their corresponding operation voltages from their optimal points. For this reason, a mismatch in current leads to a drop in efficiency. The design and manufacturing of tandem solar cells is challenging and very costly,[10,11] and current matching cannot be maintained as the solar spectrum changes, particularly under

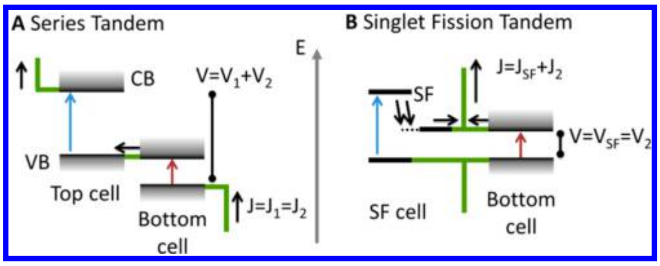


Figure 1. (A) Traditional tandem solar cell, electrically and optically connected in series. (B) Singlet fission tandem cell. The singlet fission down-conversion facilitates voltage matching by producing two low-energy excitations from one high-energy photon.

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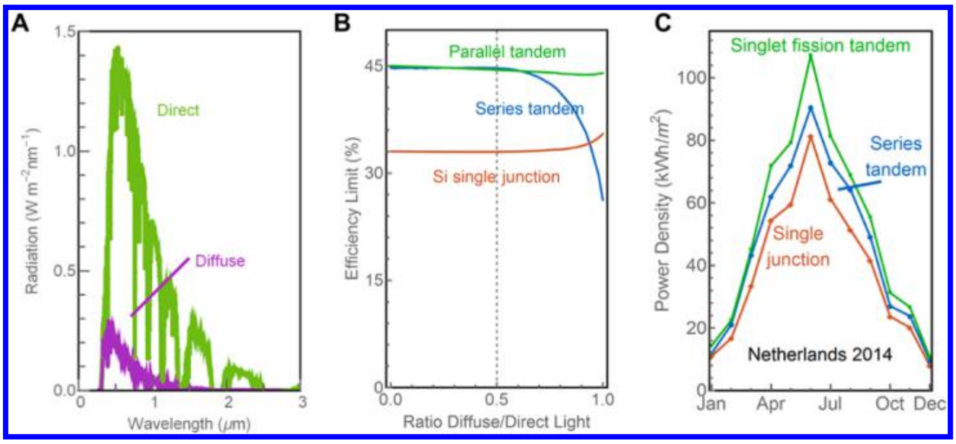

Figure 2. (A) Direct and diffuse part of the AM1.5G standard solar spectrum. (B) Calculated influence of spectral variation on the average daily efficiency limit, as a function of the direct and diffuse part of the AM1.5G standard spectrum. (C) Power density limit with spectra constructed from measured direct and diffuse irradiance in The Netherlands on different days in 2014, for an ideal cell per month of 2014. The band gap combinations of all tandem cells were optimized for the AM1.5G standard spectrum.

diffuse illumination.[12,13] As a result, tandem cells are currently limited to a small market share.[14] A monolithic tandem cell that is less affected by spectral changes could be more cost-effective and increase their contribution to the market.[15]

In contrast, when two solar cells are electrically connected in parallel, they operate at the same voltage and the currents add. Voltage scales only logarithmically with light intensity rather than linearly;[16] hence, as we show here, voltage matching is far easier to achieve for changing sunlight conditions as compared to current-matching and is more robust against fabrication constraints and materials mismatch. For conventional solar cells, the voltage is mostly determined by the band gap; hence, a two-band-gap parallel tandem configuration could not achieve voltage-matching without complex contacting schemes combining different numbers of subcells.[12] However, when the high-band-gap subcell is a singlet fission solar cell, voltage matching is possible in a single, two-terminal device.

To find the limiting efficiency for the single-junction, the conventional series tandem, and the parallel tandem configurations, we use a detailed-balance model following Shockley and Queisser.[1] This model assumes full light absorption above the band gap of the respective semiconductors and that all recombination is radiative. The main difference for the calculation of voltage-matched parallel tandem solar cells compared to conventional series tandem cells is that the generation and recombination current of both subcells adds for the complete tandem cell (see section S2 of the Supporting Information for details). In a series tandem configuration, the current of both subcells equilibrates and the voltages are added. The highest theoretical efficiency that can be reached in both series and parallel configurations is around 45% (see section S3 of the Supporting Information for details). Changes in band gap lead to smaller changes of voltage than current (see section S4 of the Supporting Information); thus, high efficiencies in a voltage-matched tandem solar cell can be achieved for a broader range of materials with different band gaps, without compromising the efficiency by limiting the absorption of the top subcell. Even when thinning of the top subcell is taken into account, the parallel tandem architecture shows higher performances for a broader range of band gaps, in particular for top cells with large band gaps (> 2 eV, see section S3 of the Supporting Information).

Crucially, the performance of a parallel tandem cell is also less affected by changing spectral conditions. The spectral shape can change because of variations of the angle between the cell and the sun, atmospheric conditions, time of the day, cloud coverage, etc.;[17] such changes alter the relation between direct and diffuse sunlight. These have different spectral shapes (see Figure 2A) due to preferential scattering of blue photons with suspended particles in the atmosphere. As a result, one of the subcells in the tandem stack receives less light than the other. Photocurrent is directly proportional to the intensity received by the subcell, while voltage changes only logarithmically. As a consequence, these changes lead to a strong current mismatch in the series configuration while creating only minor voltage mismatches in a parallel tandem configuration. To illustrate the difference between the two, in Figure 2B we show the calculated limiting efficiency for series and parallel tandem solar cell as the ratio of the direct and diffuse part change, in comparison to the single-junction efficiency. While the parallel tandem cell efficiency is constant for all conditions, the series tandem efficiency drops dramatically when the incoming light is more diffuse, well below the single-junction limit for purely diffuse light. We note that the single-junction efficiency increases at diffuse light, which is due to the fact that the diffuse spectrum is narrower than the direct spectrum. The monthly power output of an ideal series tandem, parallel tandem, and single-junction solar cell with solar spectra constructed from experimentally measured direct and indirect irradiation near Rotterdam (Netherlands) during 2014 is shown in Figure 2C (see section S2 of the Supporting Information for details). We predict that the performance of a parallel tandem cell can exceed the power conversion of a series tandem by 12% and by 33% when compared to a single-junction cell. We used the direct and diffuse spectrum from the AM1.5G standard spectrum to construct the spectra for the calculations. We note that under location-specific atmospheric conditions, the scattering may be less dominated by Rayleigh scattering (air molecules) with a stronger Mie scattering (dust, pollen, smoke, or water droplets) component, red-shifting the diffuse spectrum and reducing the overall effect. Also, more realistic models for the parallel tandem solar cells could include the specific absorption spectrum of the semiconductors involved and an electrical model.

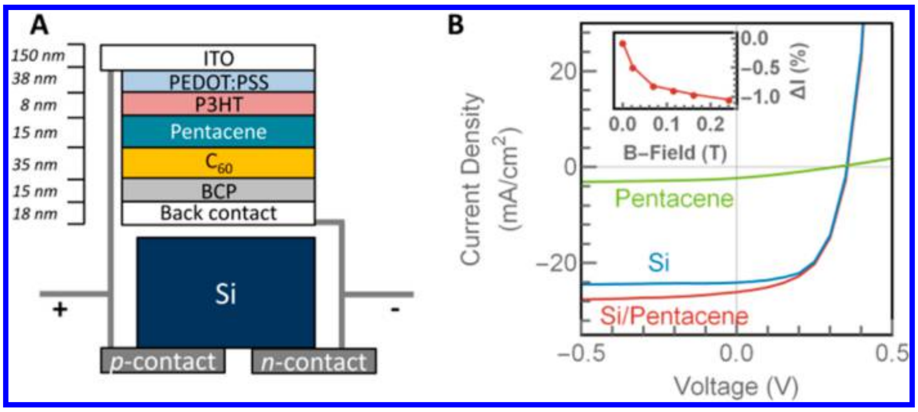

Figure 3. (A) Device architecture of the parallel tandem cell. The light, incident from above, is split into the high-energy part absorbed by the pentacene subcell and the low-energy part absorbed by the silicon cell. (B) The currents from both subcells add up at every voltage. The inset shows the change in current from the pentacene cell under an external magnetic field.

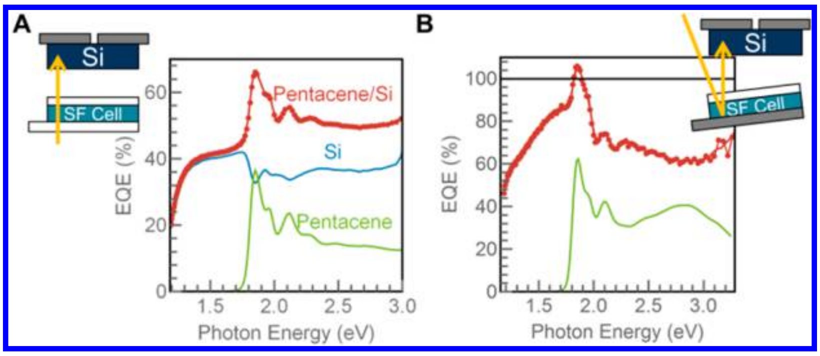

Figure 4. (A) Pentacene–silicon tandem cell with the singlet fission subcell measured in transmission. With a transparent back contact, transmitted light can pass directly through the singlet fission cell and is absorbed in the silicon cell (see inset). (B) The tandem cell with a reflective silver contact on the pentacene cell, measured in reflection. In this configuration, light passes the singlet fission cell twice before it is reflected into the silicon solar cell.

For the practical implementation of the singlet fission parallel tandem solar cell, we place a pentacene singlet fission cell on top of a silicon cell. We build the pentacene cells following previous work.[18−20] The pentacene device is made of an ITO electrode, 38 nm PEDOT:PSS, 8 nm of P3HT, 15 nm of pentacene, an electron accepting layer of 35 nm of C60, and 15 nm of bathocuproine (BCP). We use a transparent ITO front-contact and a semitransparent back-contact (LiF 1 nm/Al 1.5 nm/Ag 15 nm).[21] Thus, we can place the singlet fission cell directly in front of the silicon solar cell in such a way that high-energy photons ($E_{h\nu}$ > 1.8 eV) are absorbed in the singlet fission cell, while low-energy photons (1.1 eV < $E_{h\nu}$ < 1.8 eV) reach the silicon cell underneath (Figure 3A).

The current–voltage ($I-V$) characteristics of the two subcells measured individually (already under the singlet fission device) compared to the case where both cells are connected in parallel demonstrate current addition (Figure 3B). The overall efficiency is low (4.9% for Si, 5.1% for parallel tandem), because for practical reasons the pentacene cell was measured on top of a silicon cell with a much larger area, resulting in lower V_{OC} of the silicon cell due to a dominant dark current density and additional losses from cutting the silicon cell (see sections S1 and S2 of the Supporting Information for details). Additionally, the semitransparent silver contact on top of the pentacene cell transmits only ∼50% of the incoming light. All cells show hysteresis-free $I-V$ curves. The inset of Figure 3B shows the response of the photocurrent in the pentacene cell to an external magnetic field. The photocurrent decreases at high magnetic field because of a lower singlet-to-triplet conversion efficiency. This trend is well-understood for singlet fission solar cell devices where the photocurrent originates from triplet excitons.[18,22−24] We hence conclude at this stage that the triplet excitons generated via singlet fission contribute to the photocurrent of the singlet fission tandem cell.

In pentacene, a triplet exciton yield of 200% has been observed.[18] As a result, pentacene–C_{60} solar cells have shown very high external and internal quantum efficiencies, exceeding 100% and approaching 200% respectively.[18,25−27] To demonstrate the potential of the parallel tandem architecture to combine a singlet fission material with silicon, we measured the combined external quantum efficiency (EQE) of silicon and pentacene. The current addition is seen clearly in the EQE (Figure 4A) where the pentacene cell contributes to the current generated by the silicon cell, reaching a peak of 65% EQE at 1.85 eV (red trace). The contacts of the pentacene cell absorb around 30% of the light, and parasitic losses and reflection at the air–glass interface further reduce the amount of light reaching the silicon cell. Where the pentacene absorbs, even less light reaches the silicon cell (blue trace). Nevertheless, the pentacene peaks (green trace) are clearly visible in the EQE of the combined silicon–pentacene cell (red trace), demonstrating the contribution of carrier multiplication to the photocurrent.

Glass–air and ITO–air interfaces as well as parasitic absorption account for approximately 20% of light losses in the singlet fission device. To avoid those losses, we measure the pentacene tandem cell in a modified configuration where the singlet fission subcell features a reflective silver back-contact and is placed at a small off-normal angle from the incoming light. In this configuration, light passes through the pentacene layer twice, before and after being reflected at the back-contact, and then reaches the silicon solar cell (see inset of Figure 4B). We note that this configuration is not realistic for solar module implementation; however, it provides a useful system to enhance the absorption at the pentacene subcell and illustrates the potential of this technology. The EQE for this configuration is shown in Figure 4B. The singlet fission device clearly adds to the current, especially where it absorbs most strongly (1.85 eV). The pentacene solar cell alone produces around 60% EQE at this photon energy (green trace). The EQE of the parallel tandem cell peaks at 106% because of the very high IQE of the pentacene cell. Above unity EQE would not be possible without the singlet fission carrier multiplication process, and it has not been achieved with a two-band-gap solar cell to date.

In this work, for simplicity of construction, we have built the singlet fission solar cell independently from the silicon solar cell and connected both terminals in parallel. For future prospects of this design, the two subcells should share a common middle contact to act as a charge-collecting layer, hence reducing manufacturing costs and light absorption in the electrodes. The top electrode of the singlet fission solar cell can be connected to the bottom electrode of the silicon solar cell at the edge of the module. Alternatively, standard silicon laser drilling techniques[28] could be used to perforate the solar cell and connect the top and bottom electrodes, similar to a metal wrap-through architecture,[28] with the addition of an insulator to prevent short-circuit with the intermediate electrode.

The parallel tandem geometry would be particularly interesting for silicon solar cell configurations that already feature a conductive top contact, such as heterojunction with intrinsic thin layer (HIT) solar cells. HIT cells currently hold the world record for silicon solar cell efficiency.[29] We note that sharing the middle electrode is not possible when utilizing a standard wide-band-gap semiconductor as the top subcell in a two-terminal configuration. In such cases a three-terminal configuration is required. It is only via singlet fission that this structure can be simplified.

There has been long-standing debate over the limitation of such organic solar cells to achieve high photocurrent while keeping voltage losses low,[30] notably because of the energetic barriers to the effective formation of charge-separated states. Surprisingly, in singlet fission-based systems, such as in pentacene−C_{60}[18] and pentacene−quantum dot[7] solar cells, large photocurrents are observed with minor voltage losses (0.43 eV) with respect to the triplet level of pentacene (0.86 eV). Such small losses are comparable to those of silicon. The overall voltage is not well-matched to the voltage of an efficiency silicon cell, and if a singlet fission sensitizer with a higher triplet level is used, such as tetracene (see section S5 of the Supporting Information), larger voltages can be achieved.

In conclusion, we have shown that a voltage-matched tandem architecture in which the two subcells are optically connected in series but electrically in parallel is spectrally more stable than their series-connected counterpart. We have demonstrated an implementation of this system using singlet fission as the wide-band-gap subcell. This allows the doubling of the current from high-energy photons and reduction of the voltage to match the voltage of the low-band-gap subcell. We have realized this parallel tandem solar cell using pentacene as the singlet fission sensitizer together with a monocrystalline silicon solar cell and demonstrated that the current of the two subcells adds. We showed external quantum efficiency reaching values above 100%, something that would be impossible without the use of carrier multiplication via singlet fission.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.6b00678.

> Details about fabrication and characterization of the parallel tandem solar cells and the model used to simulate the effect of spectral changes on photovoltaic performance (PDF)

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Notes

The authors declare no competing financial interest.

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