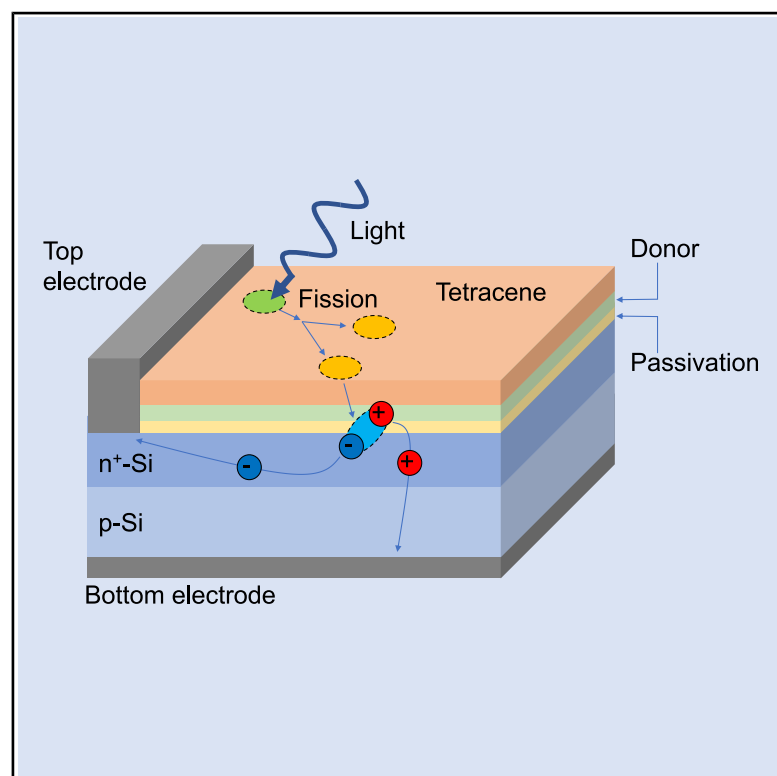


Exciton fission enhanced silicon solar cell

Graphical abstract



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In brief

Exciton fission in tetracene is coupled to silicon solar cells, enhancing the efficiency of the cells by generating more than one electron per photon in the blue-green spectrum. A thin layer of zinc phthalocyanine mediates coupling by dissociating tetracene excited states and performing sequential charge transfer to silicon.

Highlights

- Singlet exciton fission in tetracene is coupled to silicon solar cells
- Zinc phthalocyanine dissociates triplet excitons at the silicon surface
- Coupling is via sequential charge transfer rather than Dexter energy transfer
- Charge generation efficiency per photon absorbed in tetracene is (138% $\pm$ 6%)



Article

Exciton fission enhanced silicon solar cell

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CONTEXT & SCALE Silicon solar cells dominate the global production of photovoltaic energy. Their success has been driven by low-cost manufacturing and continuous efficiency improvements. But to maintain their growth, silicon solar cells will soon require new technologies that better harness light in the visible spectrum. A leading approach is to build a second solar cell, optimized for the visible spectrum, on top of a silicon cell. Unfortunately, so-called “double junctions” are more costly to manufacture and can require careful matching between the cells to maintain high performance.

An alternative solution was proposed by D.L. Dexter in 1979. He noted that exciton fission—a spin-protected process that splits the excited states of some molecules—could be used to double the performance of a silicon solar cell in the visible spectrum. His proposal promised to be relatively inexpensive to manufacture and robust under varying operational conditions because it preserves the traditional “single-junction” architecture of silicon cells.

More than 40 years after Dexter’s original proposal, this paper shows how to couple exciton fission to silicon solar cells. Molecular excited states are not transferred directly to silicon but instead dissociated into charge at the silicon surface. When the color of incident light is varied, peaks in the cell’s output current correspond to exciton fission. This confirms that exciton fission is coupled to the silicon solar cell and is successfully improving its efficiency.

New scientific and engineering challenges await this nascent technology. The promising scalability of exciton fission, however, should motivate renewed attention to an old idea that is increasingly relevant to contemporary solar cells.

SUMMARY

While silicon solar cells dominate global photovoltaic energy production, their continued improvement is hindered by the single-junction limit. One potential solution is to use molecular singlet exciton fission to generate two electrons from each absorbed high-energy photon. We demonstrate that the long-standing challenge of coupling molecular excited states to silicon solar cells can be overcome using sequential charge transfer. Combining zinc phthalocyanine, aluminum oxide, and a shallow junction crystalline silicon microwire solar cell, the peak charge generation efficiency per photon absorbed in tetracene is (138% ± 6%), comfortably surpassing the quantum efficiency limit for conventional silicon solar cells and establishing a new, scalable approach to low-cost, high-efficiency photovoltaics.

INTRODUCTION

Single-junction crystalline silicon (c-Si) solar cells are rapidly approaching their theoretical efficiency limit of 29%.¹ As in

Figure 1A, however, there are substantial opportunities to improve performance if thermalization losses can be reduced in the visible and UV spectrum. For example, using singlet exciton fission in tetracene (Tc) to double the available carriers



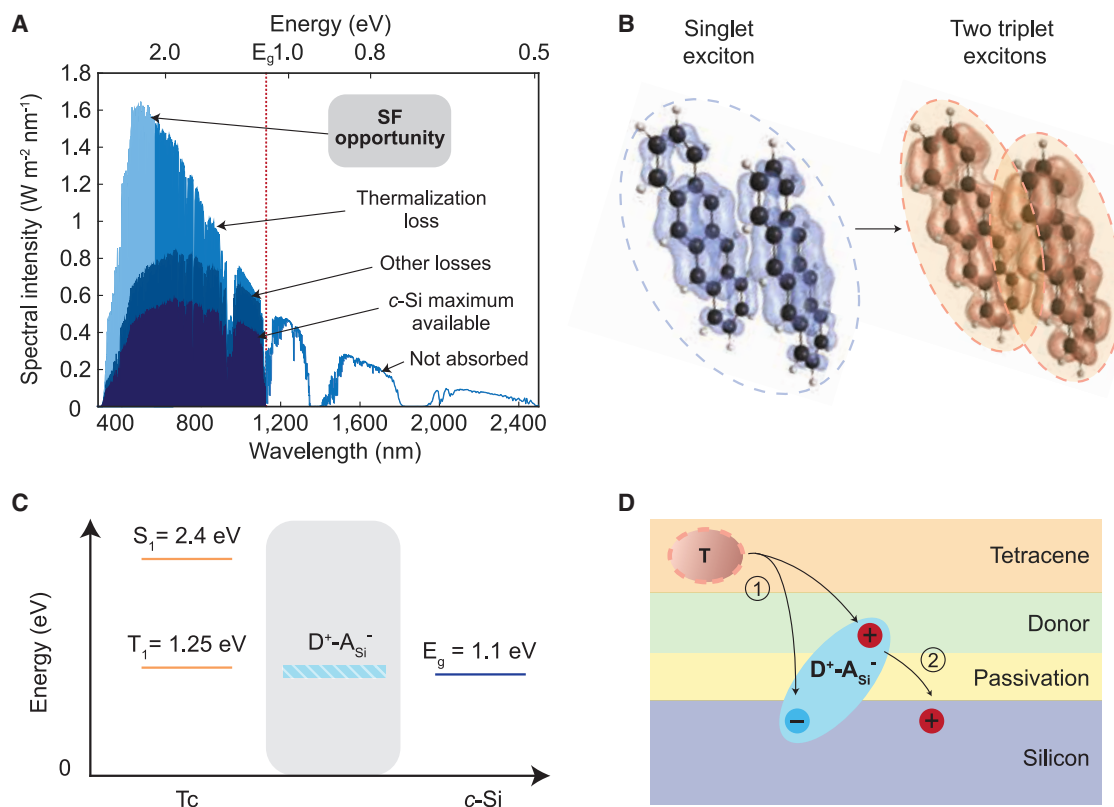


Figure 1. Singlet exciton fission and a two-part interface design for coupling to silicon

(A) The AM 1.5G solar spectrum compared with the optical absorption range of crystalline silicon (c-Si). The red dotted line indicates the band gap of c-Si. The portion of the spectrum to the right of the band gap is not absorbed. To the left of the band gap are spectral regions of the solar spectrum that are representative of energy pathways within a single-junction silicon cell at the efficiency limit. These regions correspond to photons that are available to c-Si, other losses,¹ the thermalization loss, and the opportunity for singlet fission-enhanced c-Si devices, respectively shaded from darkest to lightest blue.

(B) A molecular picture of the singlet exciton fission process, showing the difference between the attachment and detachment densities of a delocalized singlet exciton over two Tc molecules in blue, and two product triplet excitons in orange. The first excited singlet state (S_1) in Tc is the dominant pathway for optical absorption, although photons may also be captured by intermediate triplet-triplet (TT) states and higher energy singlet states.^{2,4,5}

(C) Generalized energetic requirements for the donor-acceptor state ($D^+ - A_{\text{Si}}^-$) for charge injection into silicon. The $D^+ - A_{\text{Si}}^-$ energy should ideally lie between the triplet exciton energy of tetracene (Tc) and the band gap of silicon. The specified energies for the excitonic states in Tc and the band gap of silicon presented here are experimentally obtained.⁵

(D) The two-part interface design presented in this work. The interface consists of an electron-donating layer (green) and a passivation layer (yellow). The latter passivates silicon surface defects. We propose a sequential charge-transfer mechanism: (1) the donor supports an initial electron transfer to silicon, forming $D^+ - A_{\text{Si}}^-$ (light blue oval), followed by (2) a hole transfer from the donor to silicon, ultimately resulting in triplet energy transfer to silicon.

obtained from blue and green sunlight could increase the power conversion efficiency of a single-junction c-Si solar cell to 35%.^{2,3}

Singlet exciton fission in Tc generates two spin-1 triplet excitons with energies of 1.25 eV each from one spin-0 singlet exciton with an energy of 2.4 eV⁵; see Figure 1B. Spin conservation opposes the thermalization of a singlet into one triplet exciton, protecting the process against losses and contributing to a near-ideal yield in many fission materials, including Tc.⁵ The triplet energy of Tc is just above that of the 1.1 eV band gap of c-Si, which is ideal for coupling to c-Si. However, transferring triplet excitons to c-Si and observing device enhancements has proven challenging.⁴ Depositing Tc directly onto hydrogen-terminated c-Si surfaces decreases the external quantum efficiency (EQE) of both silicon-Tc heterojunction solar cells and

interdigitated back-contacted (IBC) solar cells.^{6,7} Inserting lithium fluoride (LiF) spacers^{8,9} and pyrene passivation layers¹⁰ between the Tc and silicon also does not yield efficient triplet energy transfer. Introducing a thin interlayer of HfO_xN_y between Tc and c-Si, however, shows sensitization of c-Si by triplet excitons, albeit without demonstrating an increase in the photocurrent of an IBC cell.¹¹ The HfO_xN_y interlayer is hypothesized to play a bifunctional role, acting to passivate some silicon surface defects while simultaneously enabling triplet exciton transfer.¹¹

Here, we propose a two-component interface for efficient triplet exciton sensitization of c-Si. Our approach is guided by the apparent ineffectiveness of previous efforts to directly transfer triplets from Tc to c-Si via a Dexter mechanism.^{8,9} We instead design our cells based on the observed coupling between Tc and c-Si across thin HfO_xN_y interfaces.¹¹ We correlate evidence of

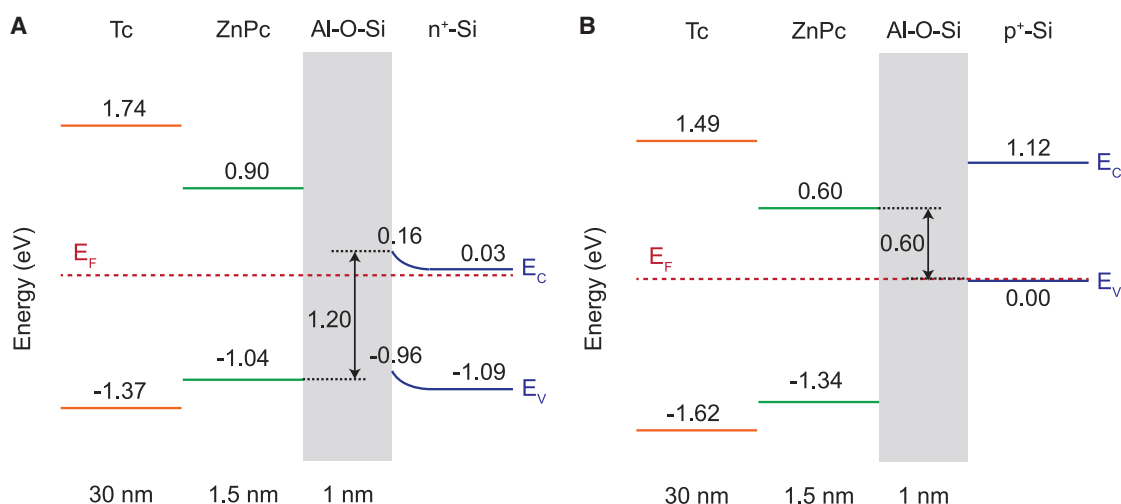


Figure 2. Energetic alignments of Tc/ZnPc interfaces on n⁺-doped and p⁺-doped c-Si

Summary of band alignments for tetracene (Tc), zinc phthalocyanine (ZnPc) and aluminum oxide (AlO_x) deposited on (A) a highly n-doped silicon surface (n⁺-Si), and (B) a highly p-doped silicon surface (p⁺-Si). The red-dashed line indicates the position of the Fermi level (E_F) of the system. The valence band maximum (E_V) and highest occupied molecular orbital (HOMO) positions with respect to E_F were measured using UV photoelectron spectroscopy (UPS). The conduction band minimum (E_C) and lowest unoccupied molecular orbital (LUMO) positions were calculated using the electronic band gaps from previous UPS and inverse photoemission spectroscopy measurements.^{11,18} The experimental energy resolution for measurements is typically 0.10 eV. The bulk E_C and E_V positions of the doped silicon were calculated from the doping concentration. The black dashed lines show the energy of the lowest-lying state at the interface between the ZnPc layer and c-Si: in (A), the electron is located on E_C and the hole is located on the HOMO of ZnPc; in (B), the electron is located on the LUMO of ZnPc and the hole is located on E_V . Nominal deposited thicknesses for the Tc, ZnPc, and AlO_x layers are listed.

triplet transfer with the presence of midgap defect states in HfO_xN_y, suggesting the possibility of sequential charge transfer via an intermediate charge-separated state supported by HfO_xN_y.¹² Consequently, we propose to mediate sensitization with an initial charge transfer to silicon,^{11,13} followed by a sequential transfer of the remaining charge carrier. One variation of this mechanism, where the electron is transferred first to silicon, results in the formation of an intermediate charge-separated state, D⁺-A_{Si}⁻, where D⁺ refers to the positively charged electron-donating material, and A_{Si}⁻ indicates the negatively charged electron-accepting role of silicon. Here, we borrow the donor-acceptor nomenclature from the field of organic photovoltaics, but note that the device architecture for our work is fundamentally different, given that the hole is also subsequently transferred to silicon. The energy of this intermediate charge-separated state should lie between the triplet energy of Tc (1.25 eV) and the band gap of silicon (1.1 eV). Tc itself is an electron donor,¹⁴ but at least in previously studied interfaces, its highest occupied molecular orbital (HOMO) is too deep to support a charge-separated state within the necessary energy range. Therefore, we propose to insert an additional electron donor at the interface with silicon that supports the D⁺-A_{Si}⁻ state with the appropriate energy, as in Figure 1C.

The second component of our interface is a thin passivation layer necessary to prevent the transferred charge carriers from immediately recombining at the silicon surface, while still enabling carrier tunneling; see Figure 1D. Aluminum oxide (AlO_x) is commonly used to passivate silicon solar cells.¹⁵ In this work, we use approximately 1-nm-thick layers of AlO_x to

both passivate the silicon surface and maintain charge tunneling across the interface.

The properties of the interfacial D⁺-A_{Si}⁻ state are unknown, particularly its binding energy. We note that D⁺-A_{Si}⁻ is unlikely to be bound due to the presence of the passivation oxide layer as well as the high dielectric constant of silicon.^{16,17} Hence, we refer to this state as a charge-separated state as opposed to a charge-transfer exciton, pending further spectroscopic characterization of its properties.

RESULTS

ZnPc as a donor material

We study zinc phthalocyanine (ZnPc) as a candidate electron-donor material (D⁺ in the D⁺-A_{Si}⁻ state) at the Tc-Si interface. ZnPc is a common donor with a reported HOMO above that of Tc.¹⁸ Our time-dependent functional theory (TDDFT) calculations (see Tables S1 and S2 and Note S1) agree with experimental studies¹⁹ that predict that the excited Tc triplet state is 0.1–0.2 eV higher in energy than the ZnPc triplet, enabling triplet harvesting at the interface²⁰ prior to the formation of a charge-separated state. Indeed, we confirm quenching of the Tc triplet exciton by ZnPc using time-correlated single photon counting (TCSPC) (see Figure S1 and Note S2). Additional calculations predict that the Tc HOMO is 0.2 eV deeper than the ZnPc HOMO. Intersystem crossing is possible in ZnPc but it is not expected to significantly influence the efficiency of silicon sensitization efficiency (see Table S3 and Note S1).

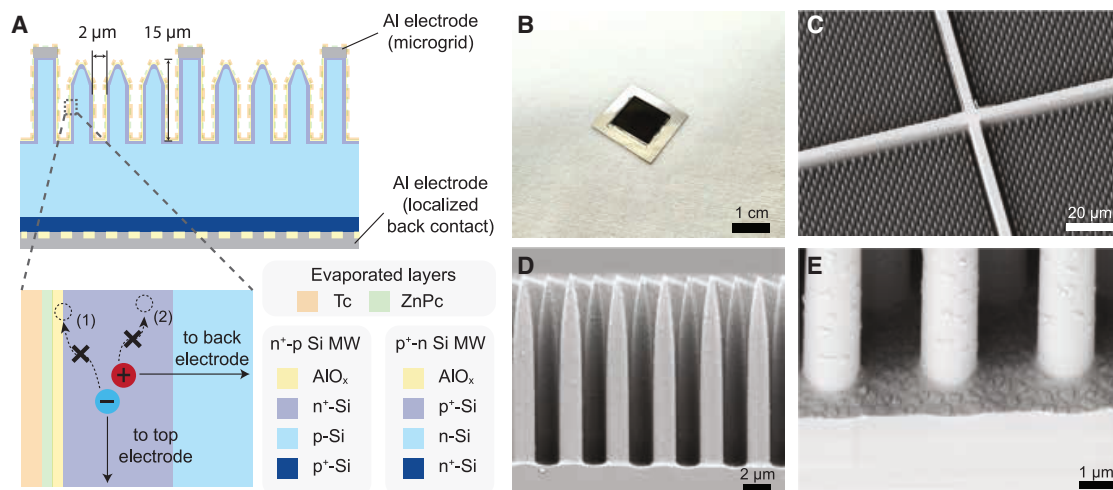


Figure 3. MW c-Si solar cells

(A) Schematic depicting layers of the microwire (MW) solar cells used in this work. MW inset shows that the solar cells are designed to extract carriers from the surface region of silicon: (1) surface recombination losses are reduced by depositing an AlO_x passivation layer; (2) bulk recombination losses are reduced by employing shallow radial p-n junctions through the MW architecture, as well as a microgrid array for the top aluminum electrode. (B) Photograph of a fabricated n^+-p Si MW cell with deposited Tc and ZnPc layers, with encapsulating glass on the active area. (C) Scanning electron microscopy (SEM) image of the Tc/ZnPc/ n^+-p Si MW cell showing a section of the microgrid array of the top electrode. (D) Transverse SEM image of the Tc/ZnPc/ n^+-p Si MW cell, showing the deposition on the MWs. (E) SEM image of the Tc/ZnPc/ n^+-p Si MW cell showing the deposition of the Tc/ZnPc layers focusing on the base of the MW cell.

We perform UV photoelectron spectroscopy to determine the energetic alignment of ZnPc at interfaces between Tc and c-Si (see [Note S3](#) and [Figures S2–S5](#) for additional details). In [Figure 2A](#), we summarize the alignments for a highly n-doped Si surface ($n^+-\text{Si}$). The difference between the c-Si conduction band minimum and the HOMO level of ZnPc is approximately 1.20 eV, within the allowed energetic range for the $\text{D}^+-\text{A}_{\text{Si}}^-$ state, as depicted in [Figure 1C](#). We neglect binding energy in the determination of the energy of the charge-separated state between the ZnPc and Si interface, $\text{D}_{\text{ZnPc}}^+-\text{A}_{\text{Si}}^-$, due to expected charge screening and delocalization in silicon.^{16,17} Here, the subscript ZnPc indicates the electron-donating role of the ZnPc. Furthermore, there is minimal barrier for subsequent hole transfer to the bulk valence band of silicon, within measurement error. We observe a negligible difference in the Tc-Si energy alignment with and without the ZnPc layer. This confirms that the presence of the ZnPc layer lowers the energy of a donor-acceptor state with silicon, thereby enabling sequential charge transfer to silicon following triplet exciton formation (see [Figure S2](#) and [Note S3](#)). In contrast, the energetic alignment with a highly p-doped silicon surface ($p^+-\text{Si}$) shown in [Figure 2B](#) exhibits a significant electron transfer barrier, and the charge-separated state is the lowest energy state in the system, hindering overall energy transfer from Tc to silicon. Thus, we suspect that the energy levels of Tc/ZnPc enable sequential charge transfer to n^+ -doped c-Si. The energetic alignment, however, is unfavorable for p^+ -doped c-Si.

Silicon solar cell design for singlet fission sensitization

Charge injection at the surface of silicon demands a solar cell design with efficient surface carrier collection. Here, we employ shallow p-n junctions, both in conventional planar geometries

and microwire (MW) solar cells that employ shallow radial junctions. Shallow junctions efficiently extract charge carriers transferred to the surface of c-Si by reducing the propagation distance of minority carriers.²¹ The MW structure also exhibits enhanced light absorption,^{21,22} particularly in the short wavelength region, reducing reflection losses.

[Figure 3A](#) shows a schematic of the fabricated devices. Following a previously reported protocol,^{23,24} we fabricate tapered c-Si MW arrays with a spacing of 2 μm and a length of 15 μm . A radial junction is formed on the p-type tapered c-Si MW arrays with an n-type emitter junction depth of 300 nm (see [Figure S6](#)) through a spin-on-dopant-based thermal doping process. To minimize recombination on the rear side, a back surface field (BSF) layer with a junction depth of 1 μm and a localized back contact is added. Then, a 1-nm-thick AlO_x layer is formed using atomic layer deposition (ALD) on the front side of the solar cell. A microgrid electrode is applied as the front electrode to efficiently collect carriers.²⁵ This microgrid electrode covers only 2% of the active area (1 cm^2), thereby reducing shading losses from the top electrodes, while also increasing the deposition area of Tc/ZnPc on the $\text{AlO}_x/\text{c-Si}$ surface. Nominally 1.5 nm of ZnPc followed by 30 nm of Tc is then thermally evaporated onto the front surface of the MW cells. For more details on the full device fabrication procedure, see the [methods](#) section.

To investigate the role of ZnPc, we also prepare a control device through an identical method on a p^+-n device where we only swap the doping of the base MW device structure ([Figure 3A](#)). [Figures 3D](#) and [3E](#) show scanning electron microscopy (SEM) images of the Tc/ZnPc/ n^+-p Si MW. Island-type growth is observed on the sides of the MWs, with similar but denser growth on the bottom region of the MW arrays. Since thermal

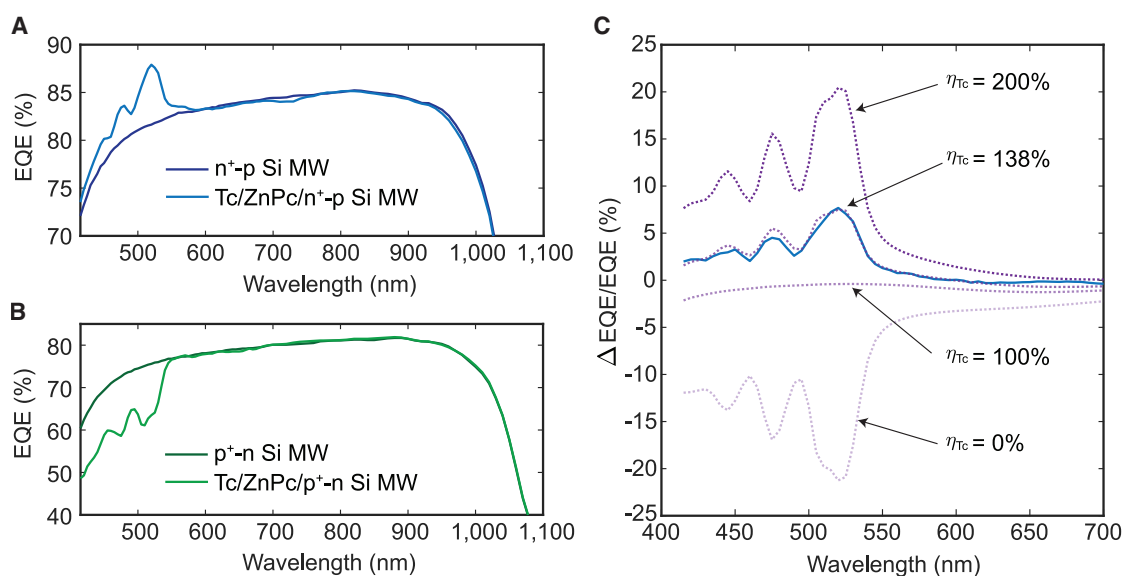


Figure 4. Device external quantum efficiencies

(A) Measured external quantum efficiency (EQE) spectra of n⁺-p Si MW cells before and after Tc and ZnPc deposition.

(B) Measured EQE spectra of p⁺-n Si MW cells before and after Tc and ZnPc deposition.

(C) Simulation fits of the percentage difference enhancement after organic deposition (ΔEQE/EQE) of the n⁺-p Si MW cells presented in (A). The dotted lines represent simulated differential EQE at different Tc sensitization efficiencies (η_{Tc}). The solid line is data for the Tc/ZnPc/n⁺-p Si MW device shown in (A).

evaporation is a directional deposition technique, increased deposition is expected to occur on the horizontal surface (bottom region) relative to the sidewalls of the MWs that are perpendicular to the deposition sources.²⁶

Device characterization

The measured EQE spectra of the n⁺-p MW device before and after Tc and ZnPc deposition are presented in Figures 4A and S7B. After deposition of Tc/ZnPc, we see a positive contribution corresponding to the absorption spectrum of Tc, with a maximum EQE increase from 81.6% to 87.9% at 520 nm. The measured J-V curves of the devices also show that depositing ZnPc and Tc on the n⁺-p MW devices results in an enhancement in the short-circuit current density, with negligible decrease in the open-circuit voltage and fill factors, resulting in an overall enhancement in power conversion efficiency, see Figure S7 and Table S4. It is notable that the introduction of molecular materials does not degrade the electrical characteristics of the silicon solar cell. Our results suggest that the role of the molecular materials in this cell architecture is primarily excitonic in nature, and other than increased charge injection, is decoupled from the operation of the junction itself.

As expected from the interfacial measurements summarized in Figure 2, p⁺-n MW devices exhibit dramatically different behavior when coupled to Tc. The measured EQE spectra before and after Tc and ZnPc deposition are shown in Figures 4B and S8B. Unlike the case with the n⁺-p MW device, we instead observe shadowing in the EQE spectra from absorption of Tc, dropping from 75.6% to 63.5% at 520 nm. This also confirms that the device performance enhancements observed in the n⁺-p devices are

not solely from enhanced antireflective effects of adding the additional organic layers.

We also fabricate n⁺-p and p⁺-n-type planar devices with random surface pyramidal texturing, which is extensively utilized in the c-Si solar cell industry for its antireflective properties. The effects on the EQE spectra are consistent with the observations in the MW solar cells presented above, although the magnitude of the enhancement is slightly decreased (see Figure S9B and Table S5).

The role of charge tunneling in the formation of the D⁺-A_{Si}⁻ state is verified by replacing the 1-nm-thick AlO_x passivation layer on an n⁺-p MW solar cell with a 10 nm-thick Al₂O₃ passivation layer. On the thicker sample, we observe Tc shadowing in the EQE spectra, demonstrating that coupling to c-Si is disrupted (see Figure S10A). We verify that ZnPc is essential by fabricating control devices without the ZnPc donor layer on both n⁺-p and p⁺-n MW devices, where we again observe Tc shadowing in the EQE spectra (see Figures S10B and S10C). We note that while both n⁺-p and p⁺-n solar cells fabricated without the ZnPc layer exhibit shadowing from Tc, the shadowing is less in the n⁺-p MW device. This suggests that there may be a small number of triplet states from Tc that are able to undergo Dexter transfer or sequential charge transfer to c-Si, potentially via charge-separated states incorporating the tail of the Tc density of states.

DISCUSSION

The overall Tc sensitization efficiency, η_{Tc}, encompasses singlet fission efficiency in Tc, transport of triplets to the interface with

silicon, triplet transfer efficiency at the interface, and extraction efficiency of charge carriers transferred to silicon. We emphasize that singlet exciton transfer alone from Tc to c-Si in the n⁺-p MW device yields a maximum sensitization efficiency $\eta_{TC} = 100\%$. Indeed, it is not possible to observe Tc peaks in the EQE of the silicon solar cell unless there is efficient ($\eta_{TC} > 100\%$) coupling to triplets generated by singlet exciton fission. To evaluate η_{TC} we perform a transfer-matrix model of the layers in our solar cell.²⁷ Calculation details are presented in [Note S4](#) and [Figure S11](#). [Figure 4C](#) shows the fitting results to the EQE percentage differential ($\Delta EQE/EQE_0$) where $\Delta EQE = EQE_{TC} - EQE_0$ and EQE_{TC} and EQE_0 are the efficiencies of the Tc and control devices, respectively. The fit yields a sensitization efficiency of $\eta_{TC} = (138\% \pm 6\%)$, where 200% is the maximum theoretical enhancement possible for a photocurrent doubling process.

Based on our results, we expect that it is possible to significantly improve the performance of singlet exciton fission-enhanced solar cells and photodetectors toward a peak quantum yield of two electrons per photon, exceeding 100% EQE, and an overall power efficiency that exceeds the conventional single-junction limit. First, technologies from advanced-node field-effect transistors can be adopted to improve the performance of the thin passivation layer. Second, conformal coating and optimized Tc growth could substantially improve the coverage of sensitizing materials on the silicon surface. Experimentally, previous studies of Tc in organic photovoltaics¹⁴ suggest that 30 nm is the optimal thickness for capturing light while minimizing triplet diffusion losses. Because the optical absorption of Tc is relatively weak, light harvesting for exciton fission could be supplemented by additional materials. Finally, although it has long been the archetype fission material for coupling to silicon, Tc has poor photostability²⁸ and will need to be replaced with a photostable analog.

In conclusion, we demonstrate efficient coupling between a silicon solar cell and singlet exciton fission in Tc, finally realizing the solar cell concept first proposed by D.L. Dexter in 1979.³ Control over the crucial interface between Tc and silicon is established by assuming sequential charge transfer mediated by a thin layer of ZnPc. The resulting observation of more than one electron per photon in a silicon solar cell provides the foundation for a new solar photovoltaic technology capable of accelerating the global adoption of renewable energy.

METHODS

Fabrication of tapered c-Si MW arrays

The photoresist dot arrays (2 μm diameter, 1 μm spacing) were periodically patterned onto the c-Si wafer using AZ-nLOF-2035 photoresist (AZ Electronic Materials) via a photolithography process. The patterned c-Si wafer was then etched by deep reactive ion etching (DRIE, Tegal 200) with 1,500 W source power, 100 W stage power, and 45 mTorr gas pressure using SF₆ (250 sccm) and C₄F₈ (150 sccm) as source gases. Following the DRIE process, cleaning was conducted using a piranha solution (3:1 mixture of sulfuric acid and hydrogen peroxide [30% w/w in H₂O]). To fabricate tapered c-Si MWs, the c-Si MWs were immersed in an HF/HNO₃/CH₃COOH solution (RSE-100, Transene) for ~10 s.

Fabrication of tapered c-Si MW solar cells

To fabricate n⁺-p-type MWs, after the fabrication of the tapered p-type c-Si MW array on the c-Si wafers, a BSF layer was formed in a tube furnace under a mixed atmosphere of O₂ (250 sccm) and N₂ (1,000 sccm) at 980°C using a boron spin-on-dopant source (B155, Filmtronics). Following the BSF layer formation, a SiO₂ layer was thermally grown on the wafer in a furnace. This SiO₂ layer was removed from the front of the substrate with a buffered oxide etchant (BOE) after the rear side was protected with photoresist (AZ4330, AZ Electronic Materials). Subsequently, an additional 200-nm-thick SiO₂ diffusion barrier was deposited on the rear side of the wafer via plasma-enhanced chemical vapor deposition (PEH-600, Sorona). Next, an emitter layer was formed in a tube furnace under a mixed atmosphere of O₂ (125 sccm) and N₂ (500 sccm) at 800°C using a phosphorus spin-on-dopant source (P509, Filmtronics). Then, after removing the oxide layer using BOE, standard clean 1 (SC1) and standard clean 2 (SC2) cleaning processes were conducted. An AlO_x passivation layer with a thickness of 1 nm was deposited on the front side of the wafer, while a 10-nm-thick Al₂O₃ layer was deposited on the rear side of the wafer via ALD (Lucida D100, NCD) and annealed under 500 sccm of a mixed gas of Ar/H₂ (v/v = 96:4) at 500°C in a tube furnace. Patterns for the microgrid electrodes and localized back contact surface were formed on the front and rear sides of the wafer, respectively, via photolithography, using AZ4330 photoresist. For electrode fabrication, the wafer was immersed in a BOE solution, and 600-nm-thick Al films were deposited on both sides of the wafer via thermal evaporation.

To fabricate p⁺-n-type MW, after fabricating the tapered n-type c-Si MW array on the c-Si wafers, the process was the same as for n⁺-p-type MW, except for the BSF and emitter formation conditions. A BSF was formed in a tube furnace under a mixed atmosphere of O₂ (125 sccm) and N₂ (500 sccm) at 860°C using a phosphorous spin-on-dopant source (P509, Filmtronics). Then, an emitter layer was formed on the front surface of the wafers under a mixed atmosphere of O₂ (250 sccm) and N₂ (1,000 sccm) at 880°C using a boron spin-on-dopant source (B155, Filmtronics).

Singlet fission top-side fabrication

Before deposition, the samples were dipped in acetone for 5 min, and then in isopropanol (IPA) for 5 min at a low sonication power. Afterward, the samples were dried with N₂ gas.

After cleaning, the samples were transferred into a nitrogen glovebox for deposition of the organic layers. ZnPc was purchased from Luminescence Technology (sublimed grade, >99% purity) and used as received. Tc was purchased from Sigma Aldrich (sublimed grade, 99.99% trace metal basis) and purified once through a sublimation and recondensation process in a three-zone tube furnace before deposition. The organic layers were deposited by thermal evaporation in a vacuum chamber at a pressure of $<1 \times 10^{-6}$ Torr. 1.5 nm of ZnPc was deposited at a 0.2 Å/s rate, followed by 30 nm of Tc deposited at a 1 Å/s rate. Thickness calibrations were obtained from ellipsometry measurements performed on planar substrates. The surface area of the MW substrates is much larger. Thus, the true area density of ZnPc (1.5 nm nominal thickness) and Tc (30 nm nominal thickness) in the MW devices is expected to be lower.

The samples were then encapsulated in a dry nitrogen atmosphere (<1 ppm O_2) with a glass slide and UV-curable epoxy. A small piece of foil was placed to protect the active area during the UV exposure for the curing step.

Photoelectron spectroscopy

Tc and ZnPc layers were deposited on AlO_x -silicon surfaces by thermal evaporation in an ultrahigh-vacuum chamber (10^{-9} Torr) connected to the analysis chamber. 1.5 nm of ZnPc was deposited at a rate of about 0.1 Å/s, followed by 20 nm of Tc at a deposition rate of about 1 Å/s. Then, UV and X-ray photoemission spectroscopy (UPS, XPS) measurements were conducted under ultrahigh-vacuum conditions (10^{-10} Torr) at room temperature. UPS utilized He I photons (21.22 eV) emitted by a discharged lamp to determine the work function of the sample and the energy position of the ZnPc and Tc HOMO with respect to the Fermi level. The experimental energy resolution for UPS is typically 0.10 eV. The position of the Si valence band maximum (E_v), hidden by the organic and AlO_x overlayers in UPS, was determined from the position of the Si 2p core level following the Kraut method.²⁹ XPS was performed using non-monochromatized Al K α X-rays (1,486.70 eV). The Fermi level reference for all measurements was determined on a clean Au surface.

Device measurements

The current density-voltage curve of the fabricated solar cells was measured using a solar simulator (Class AAA, Oriel Sol3A, Newport) under AM 1.5G illumination. The incident flux was measured using a calibrated power meter and was confirmed using a National Renewable Energy Laboratory (NREL)-calibrated solar cell (PV Measurements Date of certification: April 6, 2018; Newport calibration no, 1883; manufacturer, Newport Oriel; material, m-Si). The solar cells were measured from -1.0 to 1.0 V at a temperature of 25°C in air using a voltage scan rate of 380 mV/s. EQE measurements were performed using a 150 W xenon lamp coupled to a Newport monochromator. The light output from the monochromator was mechanically chopped at a frequency of 330 Hz and the photocurrent from the device was measured through a lock-in amplifier. The light input intensity was measured using a Newport photodetector, responsivity calibrated by Newport. The surface morphology of the solar cells was characterized by SEM (Zeiss Merlin High-resolution SEM).

Modeling

Full details on the modeling performed to fit the differential EQE are presented in Note S4. A transfer-matrix method²⁷ was used to simulate the absorption of light through the device stack. The fits were performed using custom MATLAB code.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Marc Baldo (baldo@mit.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

- All data reported in this paper will be shared by the [lead contact](#) upon request.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this paper is available from the [lead contact](#) upon request.

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AUTHOR CONTRIBUTIONS

N.N., K.L., and A.L. fabricated the singlet fission top half of the solar cells and measured the device EQE; K.L. measured the J-V measurements and performed SEM imaging to characterize the solar cells; K.L. and Y.L. fabricated the base silicon MW solar cells; X.Z. and S.L. performed the UV photoelectron spectroscopy measurements; L.P.W. performed density functional theory calculations; N.N. carried out optical modeling simulations to obtain sensitization efficiencies; A.L. and J.Z.W. performed additional spectroscopic characterization on optical samples; M.A.B., N.N., K.L., and C.F.P. conceived the research project; M.G.B., T.V.V., A.K., W.A.T., K.S., and M.A.B. supervised the experiments; N.N. took the lead in writing the manuscript with support from M.A.B. and K.L.; all authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

MIT has filed a US patent application for the two-part interlayer that names N. N., C.F.P., and M.A.B. as inventors (application no: 18/689,764) and a provisional application for the device architecture that names N.N., K.L., A.L., C. F.P., and M.A.B. as inventors (serial no: 63/596585).

SUPPLEMENTAL INFORMATION

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