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ABSTRACT

Singlet fission is one of the most promising routes to overcome the single-junction efficiency limit for solar cells. Singlet fission-enhanced silicon solar cells are the most desirable implementation, but transfer of triplet excitons, the product of singlet fission, into silicon solar cells has proved to be very challenging. Here, we report on an all optical measurement technique for the detection of triplet exciton quenching at semiconductor interfaces, a necessary requirement for triplet exciton or charge transfer. The method relies on the growth of individual, single-crystal islands of the singlet fission material on the silicon surface. The islands have different heights, and we correlate these heights to the quenching efficiency of triplet excitons. The quenching efficiency is measured by spatially resolved delayed fluorescence and compared to a diffusion–quenching model. Using silicon capped with a blocking thermal oxide and aromatic monolayers, we demonstrate that this technique can quickly screen different silicon surface treatments for triplet exciton quenching.

INTRODUCTION

The efficiency of silicon solar cells is already very close to its theoretical limit,[1] which drives the search for new concepts to increase power conversion efficiency. Next to tandem solar cells, singlet fission has emerged as a promising route to allow for higher efficiency,[2] with comparably simple implementation in solar cell devices and spectral stability under the changing environmental conditions.[3]

Singlet fission is the conversion of one singlet exciton in an organic semiconductor into two triplet excitons of roughly half the energy.[4,5] Triplet excitons are dark states that cannot transfer energy radiatively or via a *Förster* type process, only Dexter type transfer

or charge disassociation and subsequent charge transfer is possible. For an increase in power conversion efficiency, these triplet excitons need to be transferred into a lower-bandgap semiconductor cell to generate additional current. One implementation where singlet fission enhances the current of a silicon solar cell (in a narrow spectral range) relies on a tandem cell configuration. Two separate cells are optically connected in series and electrically connected in parallel.[6,7] The fabrication of these tandem solar cells would be as involved as conventional tandem solar cells. It would be more elegant to directly transfer triplet excitons into silicon, which would not require any changes to the contacts of a conventional silicon solar cell.

If the triplet excitons could be directly transferred into the low-bandgap semiconductor via charge or energy transfer, a very

simple device implementation would be possible. Such a transfer has been successfully shown for purely organic solar cells,[8] into quantum dots,[9–11] and silicon using a hafnium oxynitride (HfO_xN_y) interlayer.[12] In the last example, a single layer of the singlet fission material on top of the silicon cell absorbs the high-energy part of the spectrum, generates up to two triplet excitons per photon, and injects the energy of the excitons into silicon in an, as of yet, unspecified pathway; the injection has to proceed either via direct Dexter energy transfer,[13] where both the electron and hole are concurrently transferred into silicon, or the transfer of a single charge at the heterojunction interface. Dexter transfer is observed for triplet transfer from pentacene into PbSe quantum dots,[10] from tetracene into PbS quantum dots,[11,12] Charge transfer has been observed at multiple organic/organic interfaces,[14,15] at the organic/quantum dot interface,[16–18] and at the organic/a-Si interface with a quantum dot interlayer.[19] Several attempts to show direct transfer of excitons or charges into crystalline silicon remained unsuccessful or inconclusive,[20,21] and only recently current enhancement of a silicon solar cell using a HfO_xN_y interlayer between tetracene and silicon has been demonstrated.[12]

One major hurdle in the path toward the discovery of exciton transfer into silicon is the detection method of such transfer. Triplet excitons are "dark states," meaning that they do not emit or absorb light in the absence of strong spin–orbit coupling. The only direct optical measurement is, therefore, transient absorption spectroscopy, which has been employed to measure the charge separation dynamics at the pentacene/C_{60} interface.[22] Transient absorption at the silicon interface is considerably more challenging because the features in silicon are comparably unspecific, and the absorption in the silicon solar cell reduces the signal. Furthermore, spatially resolved studies are even more difficult,[23] and excitation densities are typically orders of magnitude above those relevant in solar cells, which makes it difficult to draw conclusions from these studies for solar cell operation.

A popular method to detect the contribution of triplet excitons to the photocurrent of solar cells is to measure the photocurrent as a function of an externally applied magnetic field.[15] The field changes the ratio of singlet excitons to triplet excitons generated from photons absorbed in the singlet fission materials. At high external fields (>100 mT), the ratio of singlets to triplets increases.[24] Thus, the photocurrent contribution from triplets decreases. This method is very accurate, but it requires fabrication of a solar cell, and the magnetic field measurements on a full solar cell device require careful separation of magnetic field effects from the singlet fission contribution and from the other layers in the solar cell stack. It is also a measurement that is typically done on bulk films, which means that each variation in the materials parameters requires the fabrication of a separate solar cell.

Similarly to the magnetic field measurement of the photocurrent of a solar cell, one can use the photoluminescence (PL) of the low-bandgap semiconductor as an indication for energy transfer. If excitons are injected into silicon, then the photoluminescence (PL) of silicon can be used to measure triplet and singlet exciton injection.[12] The change of PL with magnetic field allows one to distinguish between triplet and singlet exciton injection. However, several challenges arise: The photoluminescence quantum yield of silicon is weak and normal silicon detectors cannot be used, which complicates the measurement. Since a green laser beam excitation willalso

be absorbed in the silicon, the change of total PL from exciton injection is small, especially for thin singlet fission layers.

Recently, the external quantum efficiency has been used to study the photocurrent contribution from singlet fission materials.[12,21] If all triplet excitons are utilized for photocurrent, the internal quantum efficiency of the singlet fission materials would be close to 2, which would increase the external quantum efficiency of the silicon solar cell. So far, however, the contributions from triplet excitons could only clearly be distinguished from the noise for very efficient transfer of triplet excitons.[12] The noise level and, therefore, the error are comparably high because the method relies on accurate optical modeling of the full solar cell stack and the comparison with a reference cell. Again, this method also requires solar cell fabrication, which adds fabrication complications and additional potential for errors.

A necessary requirement for the transfer of triplet exciton energy or charge is the quenching of the triplet exciton at the organic/silicon interface. This effect was used to study exciton transfer by Piland and co-workers.[20] They deposited tetracene layers of varying thicknesses, with and without an insulating spacer layer. They used quenching of the delayed luminescence lifetime to detect any transfer of triplet excitons at the tetracene/silicon interface. Again, no clear sign of transfer was detected. This method relies on a material that shows delayed fluorescence, originating from the recombination of two triplet excitons into an emissive singlet exciton. It also requires separate samples for each thickness, and is a bulk method, without spatial resolution, while tetracene forms an intricate microstructure,[25] which influences singlet fission rates.[26]

Here, we measure the quenching of the delayed fluorescence with high spatial resolution on a silicon sample covered with many single-crystal tetracene islands of different thicknesses. We can measure the lifetime quenching for hundreds of different thicknesses in a single measurement on a single sample under the very same conditions (deposition, interface, light excitation, and collection). We use this rapid and accurate method to study the triplet transfer on tetracene/silicon samples with different interfacial surface treatments, and compare the result to a model of exciton diffusion and transfer. Despite very thin interfacial layers on silicon, and comparable passivation across surface treatments, we find no evidence for transfer of either charge or excitons into silicon. We speculate about the possible reasons and suggest a path toward efficient transfer.

RESULTS AND DISCUSSION

A necessary requirement for triplet energy transfer is the change in the delayed fluorescence as a function of distance to the interface. The photoluminescence of singlet fission materials such as tetracene commonly shows two decay components in the polycrystalline thin films, prompt and delayed fluorescence.[27] The prompt fluorescence is due to the quenching of singlet exciton recombination by singlet fission, while the delayed fluorescence stems from the recombination of two triplet excitons to form an emissive singlet state (Fig. 1). If the triplet excitons transfer across the interface, then the excitons that experience the interface during their lifetime are quenched (Fig. 2). Thus, for efficient triplet (singlet) transfer, thinner films will show a shorter delayed (prompt) fluorescence compared to thicker films.[20]
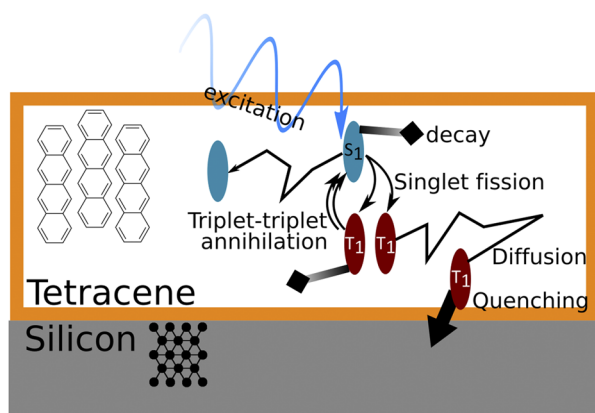
FIG. 1. Schematics of the processes included in the simulation. Excitation with a short laser pulse is followed by singlet fission in tetracene and diffusion of both singlet and triplet excitons. Singlet and triplet excitons have various non-radiative decay mechanisms that can be summarized with one decay rate. Quenching at the interface is assumed to be only present for triplets. The simulations allow us to calculate the density of singlet and triplet excitons over time. The singlet exciton density is proportional to the number of emitted photons, which is measurable in our experiment.

To simulate the effect of surface quenching on the photoluminescence we modeled the generation, diffusion, and extinction of singlet and triplet excitons. The singlet exciton density profile follows the absorption in tetracene, described by the Beer–Lambert law. Interference effects only have a small effect on the absorption profile, as shown by transfer matrix modeling in the supplementary material, Sec. S3. We follow Piland *et al.*[20] to model the generation and recombination of singlet and triplet excitons and add a 1D-diffusion term for singlet and triplet excitons. The quenching (e.g., by transfer into silicon) of triplet excitons is modeled via different boundary conditions at the tetracene silicon interface. We
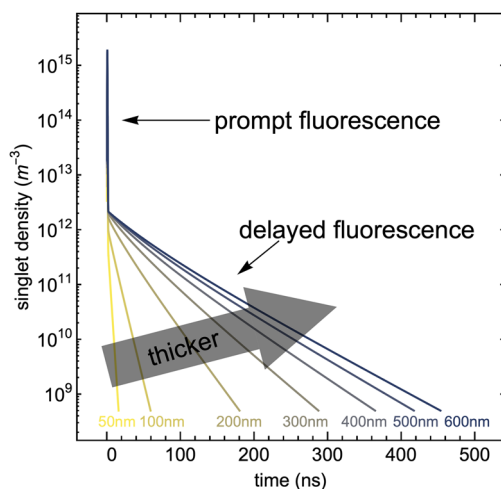
initially assume full quenching, but the model also allows us to use different quenching efficiencies (surface recombination velocities), as described in the supplementary material, Sec. S2. The photoluminescence intensity is proportional to the singlet exciton density, which allows us to predict the photoluminescence transients for tetracene islands with different thicknesses. The model shows how the delayed lifetime depends on the film thickness when assuming the perfect transfer (Fig. 2),

$$\frac{\partial S(z,t)}{\partial t} = -k_{SD}S(z,t) + k_{TS}T(z,t)^2 + excitation(t)e^{-\frac{z}{z_0}}$$
$$+ Diff_S\frac{\partial^2 S(z,t)}{\partial z^2},$$

$$\frac{\partial T(z,t)}{\partial t} = -k_{TD}T(z,t) - k_{TS}T(z,t)^2 - k_{TT}T(z,t)^2$$
$$+ \left(k_{ISC} + 2k_{fiss}\right)S(z,t) + Diff_T\frac{\partial^2 T(z,t)}{\partial z^2},$$

where S and T are the singlet and triplet exciton densities, respectively; k_{SD} and k_{TD} are the sum of all singlet and triplet decay mechanisms, respectively; and k_{TS} is the triplet annihilation to singlet decay rate. Excitation(t) is the excitation laser profile with time, multiplied with the exponential decrease of the light intensity according to the Beer–Lambert law inside the slab. $Diff_S$ and $Diff_T$ are the average diffusion constants for singlets and triplet excitons, respectively. k_{TT} is the triplet–triplet annihilation rate to higher lying triplet states. k_{ISC} is the intersystem crossing rate, and k_{fiss} is the singlet fission rate. All constants are taken from literature and are shown in the supplementary material, Sec. S2.

The prompt fluorescence lifetime is only determined by the singlet fission rate, which does not change with tetracene thickness. The delayed fluorescence becomes slower with thicker tetracene layers and levels off after 500 nm (Fig. 3).
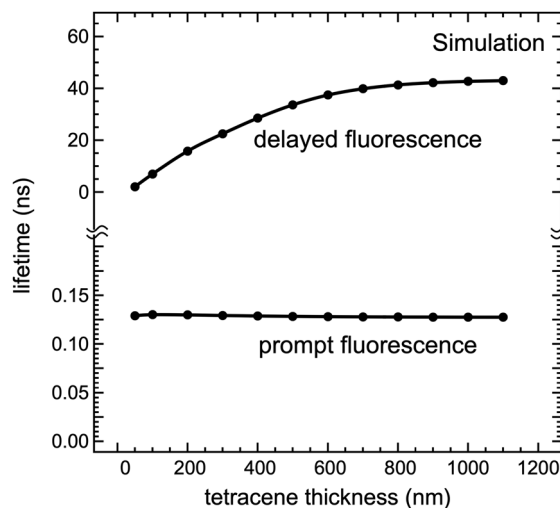
FIG. 3. Simulation of the lifetimes of a tetracene slab on top of a quenching silicon surface. The values are extracted from Fig. 2 with a single exponential fit. The delayed fluorescence describes the triplet lifetime and can be used to identify a quenching surface. After a certain thickness, the quenching surface does not influence the triplets anymore and the lifetime levels off. The prompt fluorescence is not affected by the quenching surface and stays constant.

FIG. 2. Simulation of the singlet density (proportional to the PL intensity) as a function of time for perfect triplet quenching. Different colors represent different thicknesses of the tetracene slab. The delayed fluorescence slows down with thicker tetracene layers.

Using our diffusion model, we find that the delayed lifetime should, in fact, depend on the distance to the interface, while the prompt fluorescence lifetime should be independent of that distance (Fig. S5 in the supplementary material). Note that the length-scales involved here are shorter than the length-scales at which we expect a change in optical coupling into the Si from the refractive index difference and Purcell enhancement of the lifetime because of an enhanced local optical density of states close to a semiconductor interface.

Tetracene, the prototypical singlet fission material, grows in islands on the silicon surface for nominally thin films. These presumably single-crystal islands show a range of thicknesses and can hence be used to distinguish the change in delayed lifetime for a range of distances to the surface. We note that when observing a large area of different islands, any effect of different island heights will be averaged out. Thus, here, we probe the lifetime of the islands individually by microscopically resolved photoluminescence lifetime, and correlate the delayed lifetime of each island to its height. It has been shown that morphology has an influence on singlet fission efficiency[28,29] and that the growth mode of tetracene changes from 3D to 2D growth with increasing deposition rates above a few Å/s.[25] The tetracene islands in this experiment are grown at a deposition rate of 1 Å/s for all samples, so we can assume that the growth mode stays constant between islands and between samples.

A well-performing silicon solar cell needs a good surface passivation, usually accomplished by amorphous silicon layers, highly doped layers or SiN_x passivation layers. All these layers do not allow for free access to the front side of the silicon that is necessary for direct energy transfer from tetracene directly into silicon. The close distance needed between tetracene and silicon precludes a thick passivation layer; consequently, we probe the transfer on thinner passivating layers. One such passivating interlayer is a short organic molecule that is covalently bound to the top layer of silicon atoms. It has been shown that such organic passivation layers can reach a surface recombination velocity comparable to that of good inorganic passivation layers.[30] This layer of organic molecules can also prevent the growth of a native oxide layer between tetracene and silicon. In addition to the passivation and close distance to the surface, the organic molecules could also be used to control the tetracene growth, and as a result, the tetracene crystal orientation. The orientation of the tetracene molecules on the silicon surface determines the degree of wavefunction overlap between the triplet exciton and silicon; a larger wavefunction overlap integral leads to a more efficient exciton transfer.

The alignment of the tetracene molecules at the surface depends both on the deposition conditions and on the surface energies, which can be tuned with different organic capping layers of the organic passivation. We have attached molecules consisting of four benzene rings (pyrene) as interlayers, designed to facilitate the transfer of triplet excitons, and we compare them to our reference sample of thin 2.4 nm thermally grown layers of silicon oxide, which will block the short range (<1 nm[31]) Dexter type transfer. The supplementary material contains the details of the surface modification procedure of aromatic alkynes (phenyl acetylene, 2-ethynylnaphtalene, 1-ethynylpyrene) on a hydrogen terminated silicon surface and their characterization. We use ellipsometry and XPS to measure their thickness to be between 1 nm and 1.4 nm, water contact angles

to assess their quality, and AFM to measure film roughness (see supplementary material, Sec. S1).

To measure the delayed fluorescence lifetime as a function of the island height, we mark a spot on our substrate and measure both the height of the islands by AFM and the lifetime by time-correlated single photon counting (TCSPC) microscopy. We then use an automated algorithm to overlap the measurements, find the individual islands, and compare the height and lifetime of each of the islands (Fig. 4).

We combine all pixels that make up an island in the TCSPC data to calculate the lifetime average over that island. From the AFM data of each island, we choose to use the mean of the highest 25% of pixels as a measure for the height of an island. Using the mean of all pixels yields similar results (see the supplementary material, Fig. S10).

Fitting the TCSPC data of the PL decay presents a unique set of challenges. We measure the islands microscopically; therefore, we only collect few counts in the delayed fluorescence decay, on the order of 100 photons per island in total. The decay is not mono-exponential, a fact we can already see in our model and the raw decay trace data. We found that the proper accounting of the Poissonian distribution of photons in the low count regime and the choice of a simple fitting model are critical to extract the correct correlation between the lifetime and height. Fitting the decay traces with an unsuitable method, for example, assuming Gaussian noise, can lead to correlations that are an artifact of the assumption and not the data. More insight into the lifetime fitting and a link to our fitting script can be found in the supplementary material, Sec. S6.

Plotting the delayed lifetime of each island against the height of each island allows us to detect correlations between the two. If there was efficient transfer of triplet excitons, we would expect longer delayed lifetimes at thick islands, leading to a positive slope. The results for the samples with oxide grown between the Si and the tetracene are shown in Fig. 5. The delayed lifetime is related to the slowest timescale fitted, τ_3. For the thermal blocking oxide, we find a slope of $(-3.3 \pm 3.8)\ 10^{-2}$ ns/nm. The pyrene passivation in Fig. 6 shows a slope of $(-3 \pm 2)\ 10^{-2}$ ns/nm, both compatible with the absence of any correlation between the island height and delayed fluorescence lifetime. The absence of a slope from the pyrene surface passivation techniques in Fig. 6 shows that there is either no or only very inefficient transfer of triplet excitons.

Different silicon treatments can lead to different tetracene growth modes and interface trap densities, which could affect the triplet lifetime. However, all of the tetracene islands of one sample experience the same surface and environment, which allows us to compare these islands and observe quenching for each surface.

The model we have described above allows us to simulate different quenching efficiencies; from the simulations, we can estimate that the surface quenching in these samples is smaller than 20 cm/s (Fig. S7 in supplementary material).

We note that our method cannot distinguish between the presence of quenching at the interface by triplet transfer and quenching by charge transfer, surface traps, etc. There are large differences in the silicon surface treatments and presumably trap state density. We measured the free carrier lifetime for both surface passivation methods described above to study the influence of trapping on triplet exciton lifetime (Section S7 in the supplementary material). We find
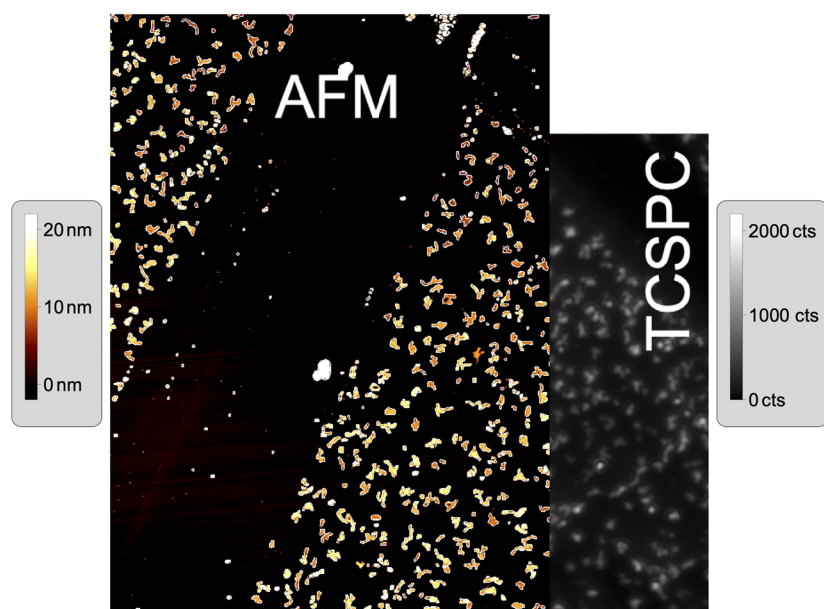
FIG. 4. Visualization of the algorithm that overlays AFM and TCSPC data and identifies islands in both datasets. Islands that are used in the analysis are marked with a white border.

no significant difference in surface passivation between samples. This measurement suggests that the triplets are reflected at the interface for all surface treatments, independent of any differences in the trap state density.

Any transfer of excitons would lead to a difference in recombination velocity, independent of the transfer mechanism. Therefore, our method cannot be used to distinguish between different mechanisms. However, the mechanism for triplet exciton transfer must be charge transfer or Dexter transfer, because Förster transfer is spin-forbidden. Dexter transfer is the correlated transfer of two electrons, where an excited-state electron from the donor transfers into the excited state of the acceptor, and a ground-state electron from the acceptor transfers into the ground state of the donor. Alternatively, the triplet excitons could be quenched by the transfer of just

one charge. Any charge transfer, including Dexter energy transfer, requires the overlap of the triplet exciton wavefunction of tetracene with the acceptor wavefunction in silicon. Wavefunctions in excitonic materials typically attenuate exponentially with distance, so that close proximity between the donor and acceptor is important. All our surface passivation layers are very thin (≤1 nm), ensuring close contact between tetracene and silicon. Another important requirement for efficient transfer is the alignment of the triplet exciton wavefunction in relation to the silicon surface. The triplet exciton in tetracene is formed mostly by the pi-orbitals, which reside on the face of the molecule. Thus, the overlap of these wavefunctions would be most efficiently facilitated by horizontal growth, where the long axis of the molecule is perpendicular to the silicon interface. We do not have a direct measurement of alignment of the first tetracene
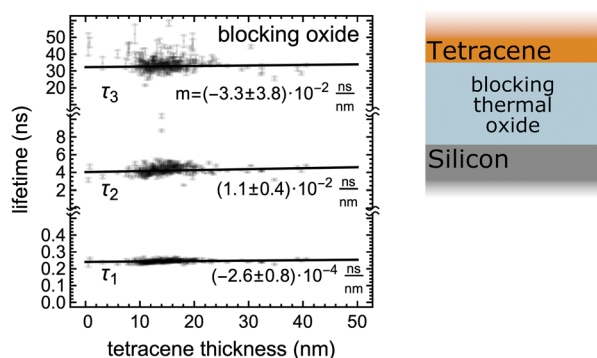
FIG. 5. The results of the lifetime fitting for the blocking thermal oxide layer. Each data point represents one island. All three exponential functions needed to fit the data do not show a slope within the error, which excludes any quenching effects at the interface.
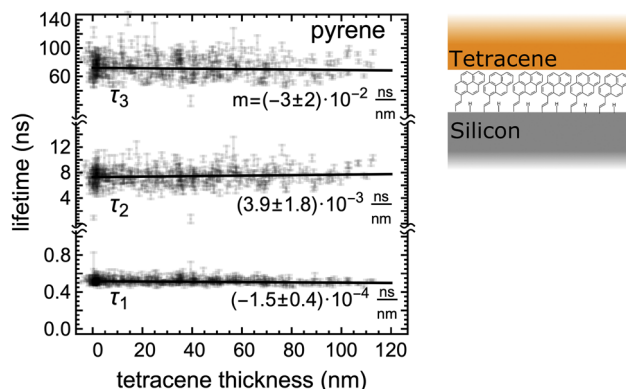

FIG. 6. Lifetimes of islands in the pyrene treated silicon surface. All three lifetime components show no slope so they are in agreement with no quenching at the surface.

molecules on the silicon surface. Different surface passivation layers likely have different formation energies, leading to different alignments of the first crucial tetracene molecules; however, we observe the absence of quenching in all cases, indicating the absence of the wavefunction overlap. We note that the exciton wavefunction on tetracene is very much localized.[32] The triplet exciton wavefunction has a theoretically calculated root mean square size of 0.35 nm,[33] experimentally measured to be 0.38 nm.[32] Therefore, it is different in nature from that of the delocalized Bloch-waves that form the silicon band structure. This difference might introduce additional inefficiencies into the transformation process between the two.

The energy of the triplet exciton (1.25 eV) is larger than the silicon bandgap (1.1 eV), but this is not the only requirement for triplet exciton transfer; the energy levels of triplet exciton in tetracene and the bands in silicon have to align with respect to vacuum. This alignment should be fulfilled in HF-etched silicon,[21] but they may misalign with our different surface passivation layers.

Since any of the bottlenecks discussed above can block the transfer of energy, it is important to develop microscopic models and measurements to investigate the rich physical system of the organic–inorganic interface. In this paper, we have described a method for sensitive quenching detection at an interface between tetracene and silicon by only using a TCSPC lifetime map and AFM height data. Correlating the delayed fluorescence and the thickness of islands with different heights allows us to detect quenching of triplet excitons. Quenching is the necessary requirement for triplet exciton transfer, which would be technologically interesting for applications in singlet fission solar cells.

SUPPLEMENTARY MATERIAL

See the supplementary material for details of the silicon surface synthesis and surface properties, for details of the exciton diffusion model, transfer matrix modeling of light absorption, and the experimental methods. The Mathematica 12 notebook used for data analysis is available on the group github page (https://github.com/HybridSolarCells).

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