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Slow light enhanced singlet exciton fission solar cells with a 126% yield of electrons per photon

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Singlet exciton fission generates two triplet excitons per absorbed photon. It promises to increase the power extracted from sunlight without increasing the number of photovoltaic junctions in a solar cell. We demonstrate solar cells with an external quantum efficiency of 126% by enhancing absorption in thin films of the singlet exciton fission material pentacene. The device structure exploits the long photon dwell time at the band edge of a distributed Bragg reflector to achieve enhancement over a broad range of angles. Measuring the reflected light from the solar cell establishes a lower bound of 137% for the internal quantum efficiency. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4858176]

Singlet exciton fission can improve the electrical yield of solar cells without increasing the number of photovoltaic junctions.[1–3] Fission increases the current from a single junction and the key measure of its efficiency is the external quantum efficiency (EQE), the fraction of incident photons that are converted into electrons and delivered to the load. Recent demonstrations using pentacene have proven that singlet exciton fission in photodetectors[4] and solar cells[5] can deliver EQEs exceeding the benchmark 100%. Insight into these devices can be gained from the internal quantum efficiency (IQE), which is the EQE corrected for the absorption of photons. The IQE is estimated to be 160% in pentacene.[5] The large difference between the internal and external quantum yield shows that light absorption is a crucial limitation in singlet fission devices. Unfortunately, it is not possible to simply use a thicker layer of pentacene because its excitons decay before dissociating into charge.[6,7] A thick layer of pentacene blended with an acceptor is also not feasible since exciton dissociation can then outcompete fission, and such architectures also exacerbate triplet-charge annihilation since excitons are kept in close proximity to charge.[8]

Light management, however, is a feasible method to improve absorption within thin pentacene layers. Enhanced absorption has been observed for structures including microlens arrays,[9] pyramidal reflectors,[10] non-planar substrates and V-shaped structures,[11] Distributed Bragg Reflectors (DBRs),[12] and plasmonic structures.[13] Almost all of these approaches require transparent/semi-transparent cathodes or growing the organic solar cell on structured substrates. In contrast, we demonstrate a simple approach for enhancing absorption in thin film organic solar cells by exploiting the slow light modes that appear at the band edge of a DBR. Using this approach, we show over a 50% enhancement in absorption and EQE of singlet exciton fission based solar cells.

The placement of the DBR between the glass substrate and the ITO anode, shown in Figure 1(a), achieves absorption enhancements in the organic solar cell without increasing the solar cell device fabrication complexity. The absorption enhancement, highlighted in Figures 2(a) and 2(b), arises due to the presence of long lived slow light modes that exist at the bandedge and the associated increase in photon density of states. The dwell time calculated from the phase change per unit frequency of the reflection coefficient of the transmission matrix is plotted as a function of wavelength is shown in Figure 2(c). We see that the high frequency bandedge mode increases the photon dwell time (effective interaction length) between the absorbing organic layers and light by a factor of 2.7. This agrees closely with the factor of 2.5 increase in absorbance observed in the solar cell with the DBR. The DBR is designed to have the high frequency band edge overlap with the spectral position of the singlet exciton absorption of pentacene. The intensity distribution for $\lambda = 670$ nm is shown in Figure 2(d), where the ITO thickness is chosen to place the intensity maximum in the spatial position of the pentacene layer. These factors result in an enhancement of the absorption at the band edge while preserving and even slightly enhancing the absorption at higher frequencies. The bottom silver mirror acts as a reflector, providing additional optical path length.

The pentacene based singlet exciton fission solar cell fabricated on top of the DBR is the high performing device of Congreve *et al.*,[5] which achieved an external quantum efficiency of 109% with an external mirror; see Fig. 1(b). The DBR featured 7.5 layers of SiN_x-SiO_2 grown via plasma enhanced chemical vapor deposition. The ITO anode was defined by a shadow mask and sputtered onto the DBR. The pentacene solar cell was fabricated following the methods described in Congreve *et al.*[5] with one exception: regio-regular P3HT (RMI-001EE) from Riekemetals was found to be an especially consistent P3HT anode material. As in previous reports, we find that a P3HT triplet blocking layer is required to obtain such high EQEs.[5,14] We observed the

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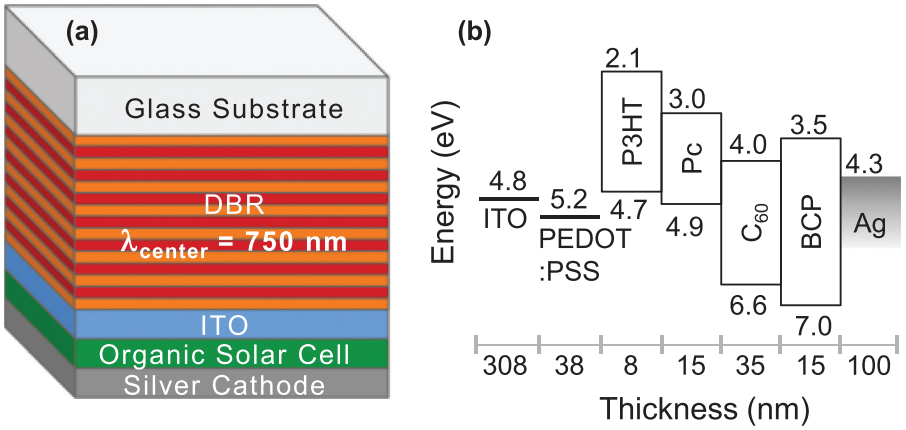

FIG. 1. (a) Schematic diagram of distributed Bragg reflector light management system and organic solar cell and (b) device structure and energy levels of the pentacene solar cell with device thicknesses in nanometers.

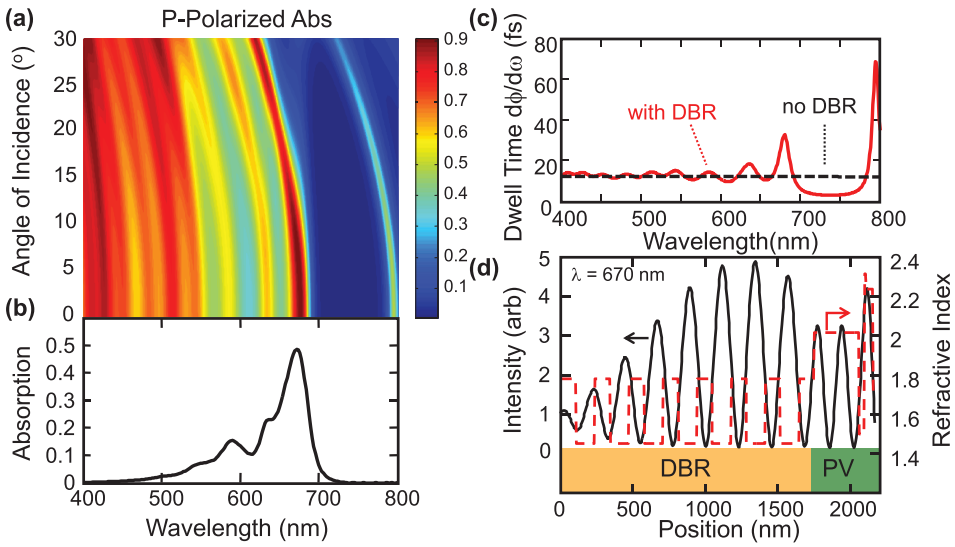

FIG. 2. Modeled p-polarized absorption of (a) the DBR enhanced solar cell as a function of angle incidence and (b) pentacene within the solar cell cavity at normal incidence without the DBR. (c) Dwell time as a function of wavelength. The solid red line corresponds to the solar cell with the DBR and the dashed black line is without. (d) Light intensity and refractive index for $\lambda = 670$ nm plotted as a function of position for the solar cell with the DBR light management system.

percentage of crystalline pentacene increases greatly relative to the bare ITO anode when poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) underneath poly(3-hexylthiophene) (PEDOT:PSS-P3HT) is used. In Figure 3, we plot the x-ray diffraction intensity versus 2θ for a 15 nm pentacene film with the PEDOT:PSS-P3HT anode and a bare ITO anode. The background amorphous x-ray scattering for each sample was subtracted using an appropriate control for ease of comparison. We clearly see significantly more diffraction from the pentacene film grown on P3HT. This suggests that non-crystalline pentacene has poor charge and/or exciton transport resulting in worse device performance. Indeed, reports of other pentacene solar cells find that PEDOT:PSS increases the crystalline content[15] and performance.[16]

Due to the dispersion of the DBR, the absorption enhancement shifts to higher frequencies for angles off normal incidence as shown in the simulated device absorption in Figure 2(a). The band edge can be spectrally tuned by tilting the device relative to the incident light. To ensure larger angular tolerance, the DBR was designed to intentionally have absorption maximum at $\lambda = 679$ nm, which is slightly red shifted from the absorption maxima of pentacene. When the DBR band-edge mode is tuned to the peak wavelength of

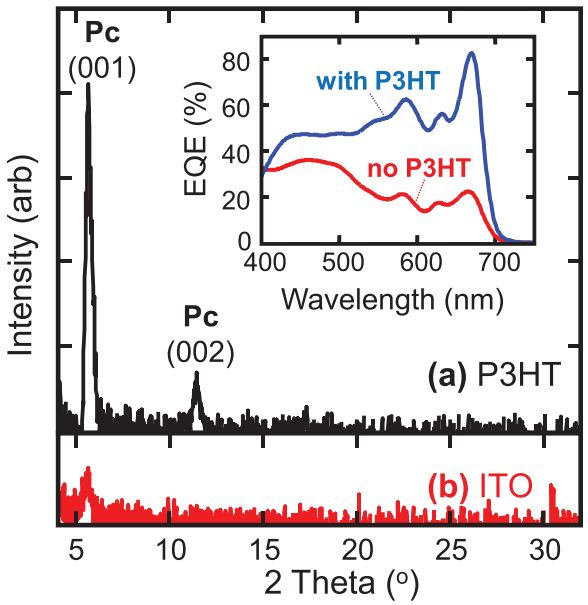

FIG. 3. X-ray diffraction intensity from a 15 nm thick pentacene film deposited on (a) the PEDOT:PSS-P3HT anode and (b) oxygen plasma cleaned ITO. Inset is the EQE of the solar cells with PEDOT:PSS-P3HT (blue) and on bare ITO (red) without a DBR light management system from Ref. 5.

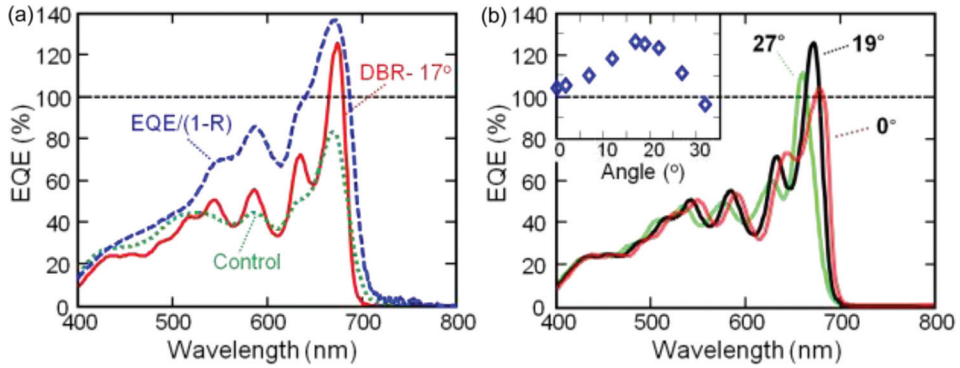

FIG. 4. (a) External quantum efficiency for a slow light DBR cavity (solid, red) at which the DBR absorption is tuned to maximize the absorption in pentacene. The control device (dotted, green) is without the DBR. The EQE divided by 1 minus the reflection (dashed, blue) provides a lower bound on the internal quantum efficiency. (b) EQE as a function of wavelength for 0°, 19°, and 27° angle of incidence on the DBR solar cell. Inset is the peak EQE as a function of angle of incidence in diamond symbols using the same y-axis.

pentacene's extinction coefficient we observe an EQE peak of 126 ± 1%, see Figure 4(a). A control solar cell, fabricated identically but without the DBR, achieved a peak EQE of only 83% and exhibited nearly zero change in EQE with angle. The DBR enhanced device demonstrated EQE greater than 100% for incident angles over the range ±27° with a relatively flat response; see inset of Figure 4(b). Device EQE measurements were performed with a spot size significantly smaller than the device area such that no light was lost from the solar cell when the device was turned.

The DBR band edge also provides a convenient way to accurately measure the minimum IQE in an organic solar cell. The conventional method for determining IQE is to measure the EQE of the solar cell and then calculate the absorption in the device, using a transfer matrix method or otherwise.[6] Measuring the absorption of the device directly is possible but properly attributing the amount of absorption occurring in each layer is difficult with losses in the metal[17] requiring special attention. As we can see from optical modeling in Figure 2(a), with the DBR the predicted absorption for the device exceeds 80% for a significant range of incident angles. In contrast, a device without the DBR has a maximum pentacene absorption of nearly 50% for normal incidence, Figure 2(b). We performed a measurement of the reflection from the device at the angle of peak EQE, eliminating the need to model the device absorption. In Figure 4(a), we plot the EQE divided by $1 - R$, where R is the reflection, and find a peak EQE/$(1 - R)$ of 137%. Including calculations of the loss of photons due to metal absorption leads to an IQE of 147%. A full transfer matrix calculation finds an IQE of 155 ± 10% across all angles of incidence, in agreement with the IQE measured previously for this device.[5]

Achieving high singlet fission efficiencies in a solar cell requires optimizing the tradeoff between insufficient absorption in thin films and exciton diffusion losses in thicker films.[6] Use of a DBR band edge mode optical structure alleviates the constraint in planar pentacene solar cells, pushing the absorption in pentacene close to 80%, and significantly simplifying the calculation of the minimum IQE. The final EQE result of 126% at $\lambda = 670$ nm should solidify singlet exciton fission as a realistic contender in the race to push mainstream solar cells beyond single junction efficiency limits.

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