Singlet Exciton Fission Photovoltaics

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CONSPECTUS

Singlet exciton fission, a process that generates two excitons from a single photon, is perhaps the most efficient of the various multiexciton-generation processes studied to date, offering the potential to increase the efficiency of solar devices. But its unique characteristic, splitting a photogenerated singlet exciton into two dark triplet states, means that the empty absorption region between the singlet and triplet excitons must be filled by adding another material that captures low-energy photons. This has required the development of specialized device architectures.

In this Account, we review work to develop devices that harness the theoretical benefits of singlet exciton fission. First, we discuss singlet fission in the archetypal material, pentacene. Pentacene-based photovoltaic devices typically show high external and internal quantum efficiencies. They have enabled researchers to characterize fission, including yield and the impact of competing loss processes, within functional devices. We review in situ probes of singlet fission that modulate the photocurrent using a magnetic field. We also summarize studies of the dissociation of triplet excitons into charge at the pentacene—buckyball (C_{60}) donor—acceptor interface. Multiple independent measurements confirm that pentacene triplet excitons can dissociate at the C_{60} interface despite their relatively low energy.

Because triplet excitons produced by singlet fission each have no more than half the energy of the original photoexcitation, they limit the potential open circuit voltage within a solar cell. Thus, if singlet fission is to increase the overall efficiency of a solar cell and not just double the photocurrent at the cost of halving the voltage, it is necessary to also harvest photons in the absorption gap between the singlet and triplet energies of the singlet fission material. We review two device architectures that attempt this using long-wavelength materials: a three-layer structure that uses long- and short-wavelength donors and an acceptor and a simpler, two-layer combination of a singlet-fission donor and a long-wavelength acceptor. An example of the trilayer structure is singlet fission in tetracene with copper phthalocyanine inserted at the C_{60} interface. The bilayer approach includes pentacene photovoltaic cells with an acceptor of infrared-absorbing lead sulfide or lead selenide nanocrystals. Lead selenide nanocrystals appear to be the most promising acceptors, exhibiting efficient triplet exciton dissociation and high power conversion efficiency.

Finally, we review architectures that use singlet fission materials to sensitize other absorbers, thereby effectively converting conventional donor materials to singlet fission dyes. In these devices, photoexcitation occurs in a particular molecule and then energy is transferred to a singlet fission dye where the fission occurs. For example, rubrene inserted between a donor and an acceptor decouples the ability to perform singlet fission from other major photovoltaic properties such as light absorption.
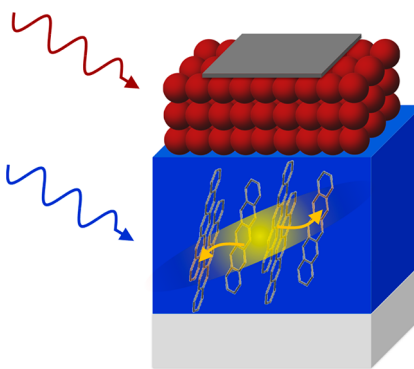
1. Introduction

Singlet fission, a process that splits a singlet (spin 0) exciton into two triplet (spin 1) excitons, promises to allow for photovoltaics with efficiencies beyond the Shockley—Queisser (SQ) limit.[6] In a conventional single-junction solar cell, an electron—hole pair photoexcited with energy above the bandgap loses its extra energy via thermalization.[7] Singlet exciton fission instead splits a high-energy excited state into two low-energy states, generating one extra exciton per absorbed photon, which would have been otherwise wasted as heat.

Although the transition between singlet and triplet states is disallowed by the conservation of spin symmetry, a pair of triplets can have some singlet character;[8] therefore, singlet fission, the conversion of a singlet into a pair of triplets, can be a spin-allowed process.[6] If the energy of the
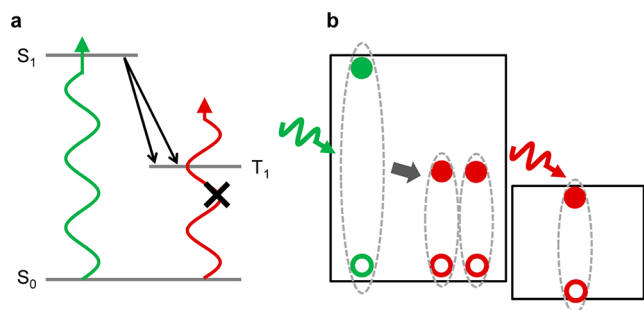
FIGURE 1. (a) Energetic structure and state transition in singlet fission materials. Photoexcitation of singlets splits into pairs of triplet states. The wavelength range between the singlet and triplet states is not optically accessible. (b) A device structure example of singlet-exciton-fission-based solar cells. The donor layer performs singlet fission, where a high-energy photoexcitation splits into two triplet excitons. The acceptor layer absorbs low-energy photons and has a bandgap similar to the triplet energy of the donor.
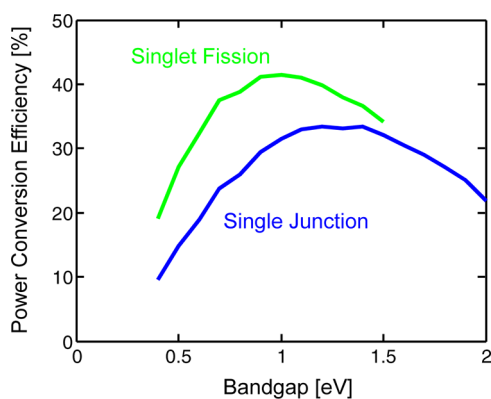

FIGURE 2. Theoretical maximum power conversion efficiency as a function of bandgap (S_1-S_0 for single junction; T_1-S_0 for singlet fission) for single junction (blue) and singlet fission (green) solar cells. To calculate the maximum efficiency of singlet fission solar cells, we followed Shockley−Queisser's theory[7] while assuming that two excitons are generated upon photoexcitation with energy greater than twice the bandgap.

singlet exciton is higher than or comparable to twice the energy of the triplet, singlet fission can be very fast, outcompeting other decay channels, including prompt fluorescence.[6]

The triplet excitons produced by fission have roughly half the energy of the initial singlet excitation. Consequently, fission limits the open circuit voltage of the cell to no more than half its previous value. Triplet excitons are, however, also dark states; the absorption in the spectral region between the singlet and triplet excitons is spin-forbidden. This empty absorption region must be filled by adding another material that captures low-energy photons, see Figure 1a. Otherwise, the singlet-fission photovoltaic system will double the photocurrent but also cut the voltage by half, leading to no net benefit in the power conversion efficiency.

See Figure 1b for an example of device structures featuring singlet fission donors and low bandgap acceptors. As shown in Figure 2, singlet fission solar cells with absorption in the singlet−triplet gap can bring the SQ limit to 41% from 33% of conventional single-junction solar cells.[6,7]

2. Pentacene-Based Solar Cells

In pentacene, singlet fission occurs exothermically since the energy of the singlet exciton, $E(S_1) = 1.83$ eV, is slightly higher than twice the triplet energy, $E(T_1) = 0.86$ eV.[9,10] Singlet exciton fission in pentacene has been observed to occur extremely rapidly, on the order of 80 fs.[9,11−15] The ultrafast nature of singlet fission in pentacene enables the efficient conversion of a singlet into two triplets in a photovoltaic device because singlet fission can outcompete or match other decay channels such as singlet exciton dissociation into charge. Indeed, several researchers have observed high external and internal quantum efficiency from pentacene-based photovoltaic cells.

The first high-efficiency pentacene/C_{60} solar cells were reported by Yoo et al., exhibiting high peak external quantum efficiencies (EQEs) up to 69%.[16,17] Their device structure was indium tin oxide (ITO)/pentacene (50 nm)/C_{60} (50 nm)/bathocuproine (BCP; 6 nm)/Al. Figure 3 displays their EQE spectrum and its analysis. Optical interference modeling revealed that the internal quantum efficiency (IQE), defined as the external quantum efficiency divided by the absorption of active layers, was 85% for pentacene absorption,[16] see Figure 3c. While not considering the possibility of singlet fission, the authors determined the exciton diffusion length of ∼70 nm for pentacene thin films.[16]

Subsequent work by Pandey et al. demonstrated EQEs as high as 83% in bulk heterojunction solar cells based on pentacene and *N,N′*-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-$C_{13}H_{27}$).[18,19] A 100-nm-thick blend of pentacene and PTCDI-$C_{13}H_{27}$ in the ratio of 3:1 (by wt %) was grown on ITO anodes covered with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). The cathode was 8 nm BCP/60 nm Ag. The blend device delivered the maximum EQE of 83%,[18] see Figure 4 for the EQE spectrum. The optical modeling shows that the absorption of active layers at $\lambda = 670$ nm is around 80%,[19] indicating that the IQE is close to 100%.

Lee et al. reported an organic multilayer photodetector based on pentacene with the peak EQE reaching 100%.[1] This device is composed of alternating 2-nm-thick pentacene and 1-nm-thick C_{60} layers; see Figure 5b for the device structure. The narrowness of each layer makes the efficiency
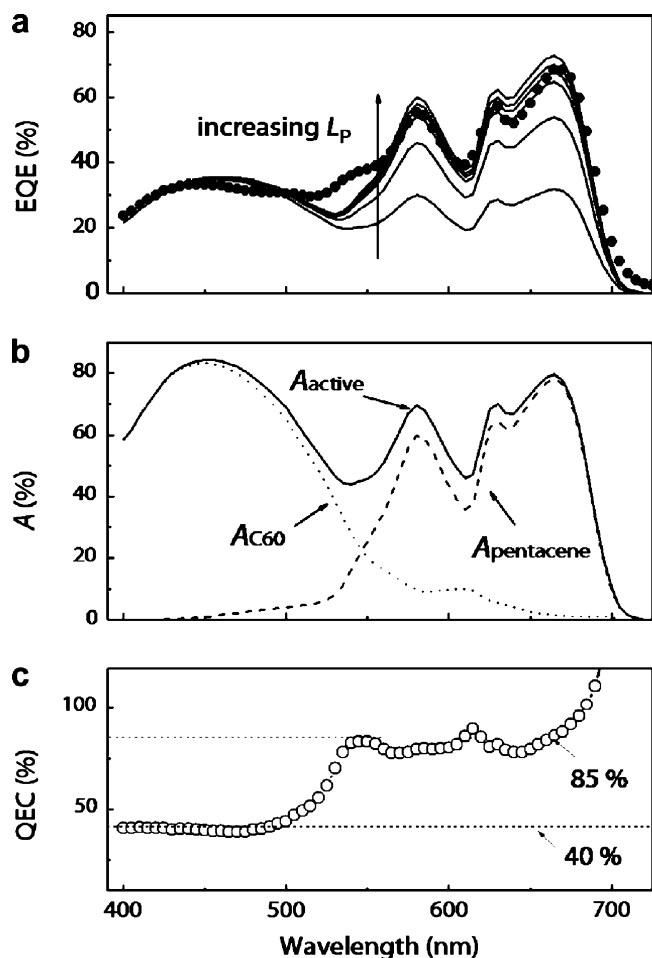
FIGURE 3. External quantum efficiency of pentacene/C_{60} bilayer solar cells. The device structure was ITO/pentacene (50 nm)/C_{60} (50 nm)/BCP (6 nm)/Al. (a) Measured (circle) and calculated (solid) external quantum efficiency with pentacene exciton diffusion lengths of 20, 40, 60, 70, 80, and 100 nm (from bottom to top). (b) Calculated absorption by both active layers (solid), absorption by pentacene layers (dashed), and absorption by C_{60} layers (dotted). (c) Internal quantum efficiencies (IQE), defined by the ratio of EQEs and absorption. Note that the IQE of pentacene is roughly double that of C_{60}. This may reflect the presence of singlet exciton fission, although differences in exciton diffusion lengths in the two materials may also be influential. Courtesy of Yoo et al. Reproduced from ref 16 with permission from Elsevier.

of exciton diffusion and charge collection under a high reverse bias close to a unity,[20] allowing the effective quantification of the yield of singlet fission inside photovoltaic cells.

Figure 5c shows the EQE spectrum of the pentacene multilayer photodetector under a reverse bias, sufficient to pull nearly every carrier out of the device.[1] The peak efficiency at $\lambda = 670$ nm is 100%. By fitting the EQE spectrum with the absorption calculated by optical interference modeling,[21] the internal quantum efficiencies (IQEs) were found to be 128% ± 2% and 89% ± 4% for pentacene and C_{60}, respectively.[1]
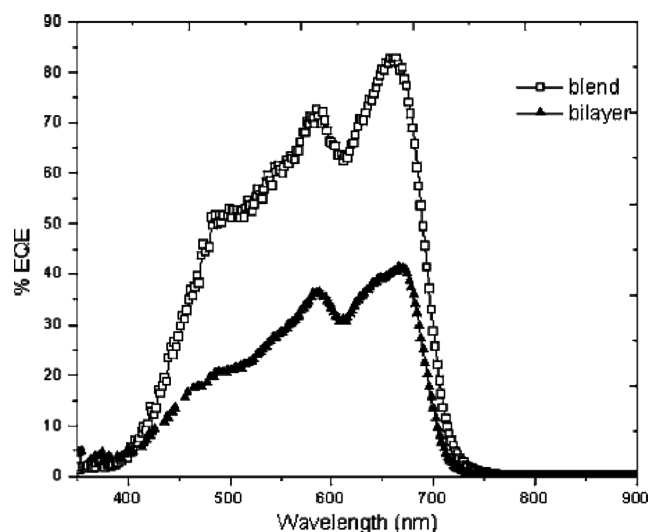

FIGURE 4. External quantum efficiency spectra for blend (□) and bilayer (▲) devices. The active layers were 100-nm-thick pentacene/PTCDI-$C_{13}H_{27}$ (3:1) blend and pentacene (45 nm)/PTCDI-$C_{13}H_{27}$ (45 nm) layers for blend and bilayer devices, respectively. Courtesy of Pandey et al. Reprinted with permission from ref 18. Copyright 2006 American Institute of Physics.

Magnetic-field-induced modulation of the photocurrent can be used to probe the efficiency of singlet fission in a singlet fission device. Under Johnson and Merrified's theory, the singlet character of the various triplet-pair states is redistributed under a magnetic field;[22] the modulation of singlet character affects the rate of singlet fission.[23] The triplet-pair state, where each triplet can have three different spin states, has nine spin configurations. In the absence of magnetic field, three configurations out of nine have a singlet character.[24] The angle between neighboring molecules affects how the number of states with singlet character changes under a magnetic field. For molecules aligned in parallel (e.g., tetracene or pentacene), when an intermediate magnetic field ($H < 0.1$ T) is applied, the singlet character is redistributed over six states, accelerating a singlet fission process.[24] Under a high magnetic field ($H > 0.2$ T), only two configurations have singlet character, slowing down singlet fission.[8,24] See ref 25 for the magnetic field effect in a molecule pair with different orientations. Note that this unique behavior of a fission process under a magnetic field can be used to distinguish singlet fission from other magnetic field dependent processes that may happen in organic photovoltaic cells, such as triplet-charge annihilation.

Figure 5d shows the magnetic field modulation in photocurrent for the selective illumination of pentacene ($\lambda = 670$ nm) and C_{60} ($\lambda = 408$ nm).[1] Under a magnetic field of $H > 0.2$ T, the photocurrent upon photoexcitation of
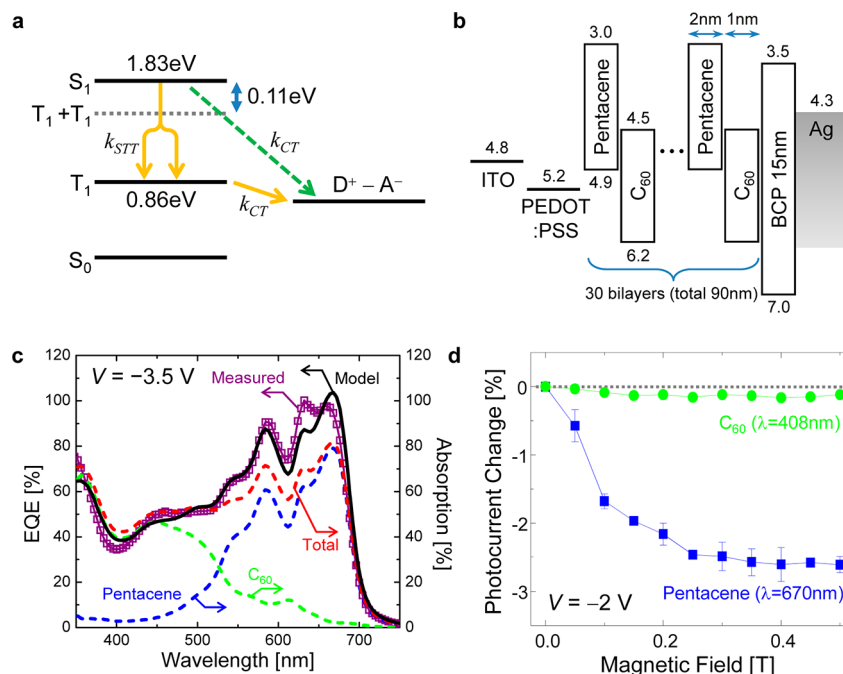
FIGURE 5. (a) An energy transfer process in a pentacene/C_{60} heterojunction. Singlet fission (k_{STT}) is followed by charge transfer (k_{CT}) of triplets, creating two charges (yellow line). Charge transfer directly from singlet states can occur and compete with singlet fission, generating only one electron (green dashed line). (b) Device structure of a pentacene/C_{60} multilayer photodetector. (c) Measured (□) and modeled (—) EQE spectra of a multilayer pentacene/C_{60} device under applied bias of $V = -3.5$ V. The absorption (dashed lines) of pentacene, C_{60}, and both layers are acquired using optical interference modeling. The IQE for pentacene and C_{60} was found to be 128% ± 2% and 89% ± 4%, respectively. (d) Change in photocurrent under varying applied magnetic field at a voltage of −2 V. Pentacene and C_{60} were selectively excited at $\lambda = 670$ nm and $\lambda = 408$ nm, respectively. Reprinted with permission from ref 1. Copyright 2009 American Institute of Physics.

pentacene decreases by up to −2.7%. Quantitative modeling of the magnetic field effect allows determination of the singlet fission yield. The modulation of fission rate is expressed as $k_{STT}(H) = \chi(H)k_{STT}^0$, where $\chi(H)$ is the modulation of the zero-magnetic-field fission rate, k_{STT}^0. According to the schematic shown in Figure 5a, the quantum efficiency enhancement factor is

$$I(H) = 2\frac{\chi(H)k_{STT}^0}{\chi(H)k_{STT}^0 + k_{CT}} + \frac{k_{CT}}{\chi(H)k_{STT}^0 + k_{CT}} \quad (1)$$

where the first term represents the number of excitons generated after undergoing singlet fission and the second term represents the number of singlet excitons directly dissociated into charge before singlet fission.[1]

The change in photocurrent is given by $\delta = (I(H) - I(0))/I(0)$. Using $\delta(H = 0.4 \text{ T}) = -2.7\%$, measured in the experiment, and $\chi(H = 0.4 \text{ T}) = 0.85$, gained from the magnetic-field-induced change in prompt fluorescence in tetracene crystals,[1,26] one predicts singlet fission to improve the quantum efficiency by 145%.[1] From the EQE modeling, the ratio of the IQEs of pentacene (128% ± 2%) and C_{60} (89% ± 4%) suggests that the pentacene singlet excitons are multiplied by 145% ± 7%, which agrees with the estimation from the magnetic field effect.[1]

3. Triplet Dissociation at Pentacene/Acceptor Heterojunction

The dissociation of pentacene triplets into charge at the pentacene/C_{60} interface has been studied by pump−probe spectroscopy[27] and time-resolved second harmonic generation (TR-SHG) spectroscopy.[15] Rao et al. probed the kinetics of triplet excitons and charges in pentacene/C_{60} bilayer films by employing transient absorption spectroscopy.[27] In Figure 6a, the photoinduced absorption (PIA) signal integrated over the probe wavelengths of 810−910 nm corresponds to the triplet states and charges, although the contribution from triplets dominates. The electroabsorption (EA) signal comes from the electric field generated by charge generation at the heterojunction.[27] The population of charges (the EA signal) grows over 2−10 ns as the number of triplets (the PIA signal) decreases.[27]

Chan et al. probed transient charge transfer dynamics at the pentacene/C_{60} junction by performing TR-SHG experiments, which detect the local electric field created by electron−hole pairs, see Figure 6b.[15] The kinetics of triplet populations at the pentacene/C_{60} interface was also measured by two-photon photoemission (2PPE) spectroscopy.[15]
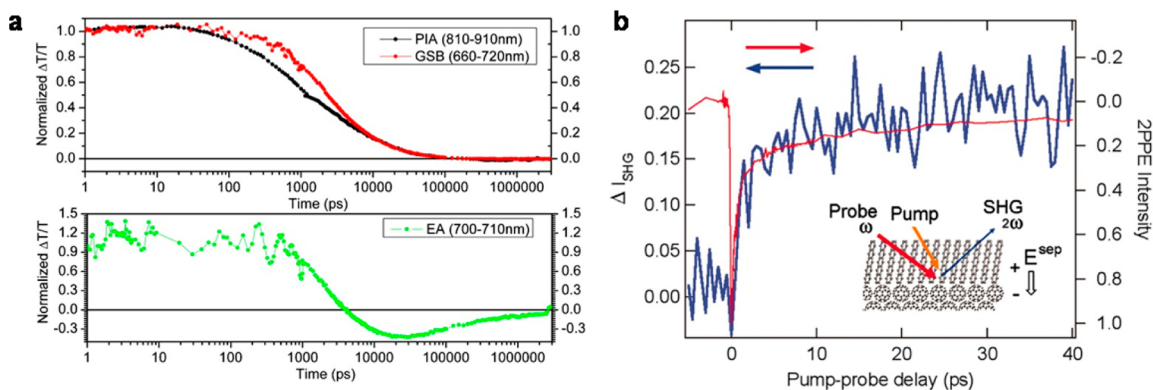
FIGURE 6. (a) Transient absorption dynamics of pentacene/C_{60} bilayers. The decay of the photoinduced absorption (PIA) averaged over the probe wavelengths of 810–910 nm (black) is attributed to the decrease of triplet populations. The electroabsorption (EA) signal (green), created by charge generation at the heterojunction, grows as the PIA signal decays. Courtesy of Rao et al. Reproduced from ref 27. Copyright 2010 American Chemical Society. (b) Second harmonic generation (SHG) intensity (blue) as a function of pump–probe delay from a pentacene/C_{60} bilayer film. SHG probes the transient electric field, established by charge transfer at the donor–acceptor interface. Also shown is normalized two-photon photoemission signal (red) of the triplet state population at pentacene/C_{60} bilayers. Courtesy of Chan et al. From ref 15. Reprinted with permission from AAAS. Data shown in both panels a and b suggest that the populations of electrons and holes grow at the same rate as the triplets decay.
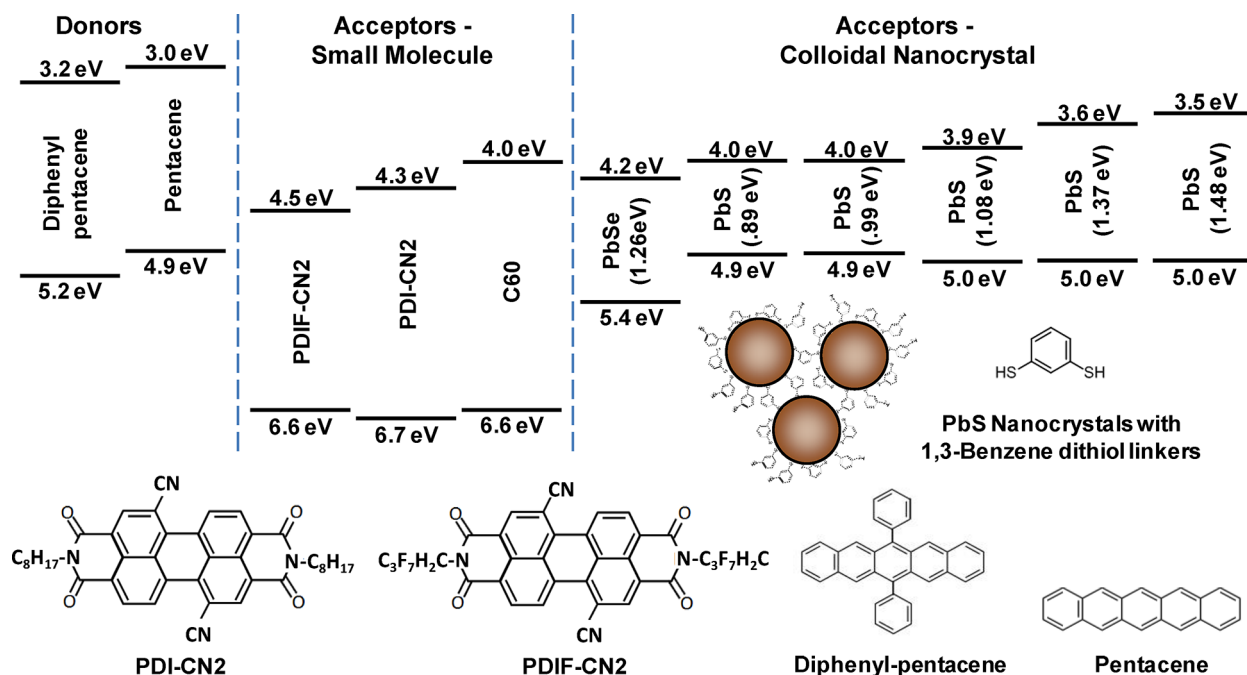

FIGURE 7. A summary of the energy levels and molecular structures used in the study on triplet exciton dissociation by Jadhav et al. Reprinted from ref 3 with permission from John Wiley and Sons.

The comparison of TR-SHG and 2PPE signals shows that the charges are created at the same rate as the decay of triplets.[15] Note that the charge generation in this work occurs within a few picoseconds, much faster than what Rao et al. observed. It is because the pentacene layer used by Chan et al. was almost a monolayer, whereas Rao et al. used 150-nm-thick pentacene films, which require triplet diffusion over longer distances.

Jadhav et al. and Ehrler et al. probed the dissociation of pentacene triplet excitons in devices by changing the HOMO level of donors and the LUMO level of acceptors,[3,5] see Figure 7. Collectively, three classes of acceptors were examined in these studies: fullerenes, perylene diimides, and lead selenide (PbSe) and lead sulfide (PbS) nanocrystals (NCs). Jadhav et al. also used two types of pentacene molecules to vary the ionization potential of donors: unsubstituted pentacene and diphenyl-pentacene (DPP).[3]

First, triplet exciton dissociation at pentacene/C_{60} interfaces was investigated by examining the contribution from
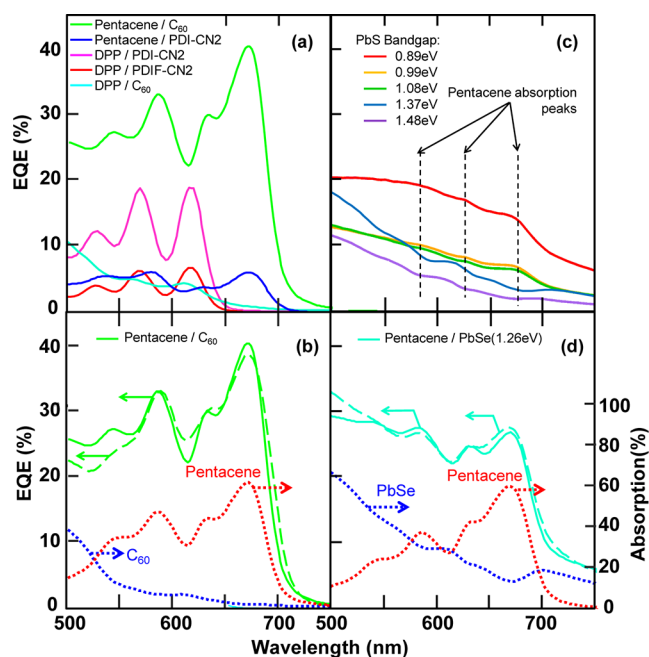
FIGURE 8. (a) Measured EQEs of small molecule acceptor devices. (b) Measured (solid) and calculated (dashed) EQEs of a pentacene/C_{60} device. Absorptions from pentacene and C_{60} layers are plotted together. Optical modeling finds that the IQE of pentacene is 63%. (c) Measured EQEs of pentacene/PbS nanocrystal devices. (d) Measured (solid) and calculated (dashed) EQEs of pentacene/PbSe nanocrystal devices. The IQE of pentacene is determined to be 35%. Reprinted from ref 3 with permission from John Wiley and Sons.

FIGURE 9. Photocurrent changes under magnetic fields for various donor–acceptor multilayer devices. Reprinted from ref 3 with permission from John Wiley and Sons.

pentacene in EQE spectra, see Figure 8a. It is notable that the DPP/C_{60} junction generates very little current from photoexcitation of DPP relative to pentacene in junctions with C_{60}. Because DPP has a slightly deeper HOMO than pentacene (5.2 ± 0.1 vs 4.9 ± 0.1 eV, respectively), the tentative conclusion is that triplets in DPP cannot break up into charges due to the high barrier to charge transfer states.[3] Indeed, when DPP is paired with acceptors with deeper LUMO, such as *N,N*'-dioctyl-6,12-dicyano-3,4,9,10-tetracarboxyperylene diimide (PDI-CN2) and *N,N*0-1*H*,1*H*-perfluorobutyl dicyanoperylenecarboxydiimide (PDIF-CN2), charge transfer from triplets starts to work again.

Second, the polarity of the magnetic field effect on photocurrent can be employed to probe the dissociation of triplets.[3] As shown in Figure 9, pentacene/C_{60} and DPP/PDIF-CN2 junctions, which convert triplets into charges efficiently, show a negative magnetic field effect in the photocurrent, because singlet fission slows down under a magnetic field and fewer charges are formed. On the contrary, the DPP/C_{60} interface, where the triplet dissociation is disabled, exhibits a positive magnetic field effect. The reduced rate of singlet fission under applied magnetic field results in more singlet
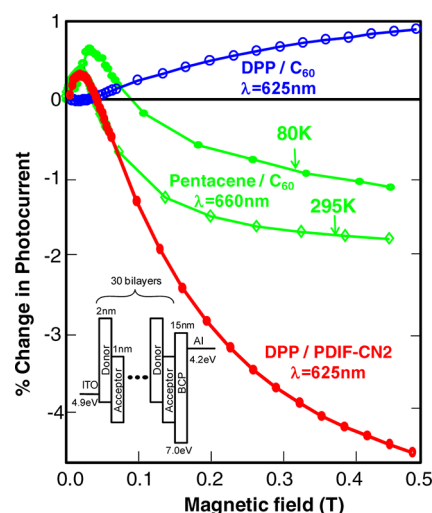
excitons, leading to more charges at the junction where triplets cannot be dissociated.[3]

Beyond the archetypal pentacene/C_{60} junction, Jadhav et al. and Ehrler et al. both studied junctions between pentacene and infrared-absorbing NCs.[3,5] Figure 10a shows the pentacene/PbSe NC device structure and the EQE spectra with varying NC bandgaps in ref 5. The presence of the pentacene absorption in the EQE means that the excited state in pentacene has sufficient energy to dissociate at the donor–acceptor heterojunction.[5] By detecting the pentacene contribution from the EQE data, Ehrler et al. showed that the pentacene triplet energy is at least 0.85 eV and at most 1.00 eV in operating devices.[5] As shown in Figure 8c,d, Jadhav et al. observed a similar phenomenon in the EQE of pentacene/PbS NC devices with varying NC LUMO levels.[3] The contribution to photocurrent from pentacene absorption changes from positive to negative as the LUMO level of the acceptor increases.

Figure 11 summarizes the relations between the CT energy and the effectiveness of triplet dissociation.[3] The junctions dissociating triplets are colored in blue, and those not dissociating are represented in red. It was found that the pentacene/C_{60} interface is sensitive to small changes in the donor and acceptor energy levels, suggesting that pairing with proper acceptors is significant when studying pentacene derivatives.[3]

Theory also suggests that the pentacene/C_{60} junction is capable of dissociating pentacene triplet excitons. Yost et al. calculated the charge transfer (CT) state using constrained density functional theory.[3,28] As shown in Figure 12, the CT

FIGURE 11. $E_{LUMO,acceptor} - E_{HOMO,donor}$, approximate energy of charge transfer states, for various donor−acceptor heterojunctions. Blue indicates that the EQE measurement and magnetic field effects in photocurrent confirmed the dissociation of triplets of those junctions, while red means that triplets cannot be separated into charges. Reprinted from ref 3 with permission from John Wiley and Sons.
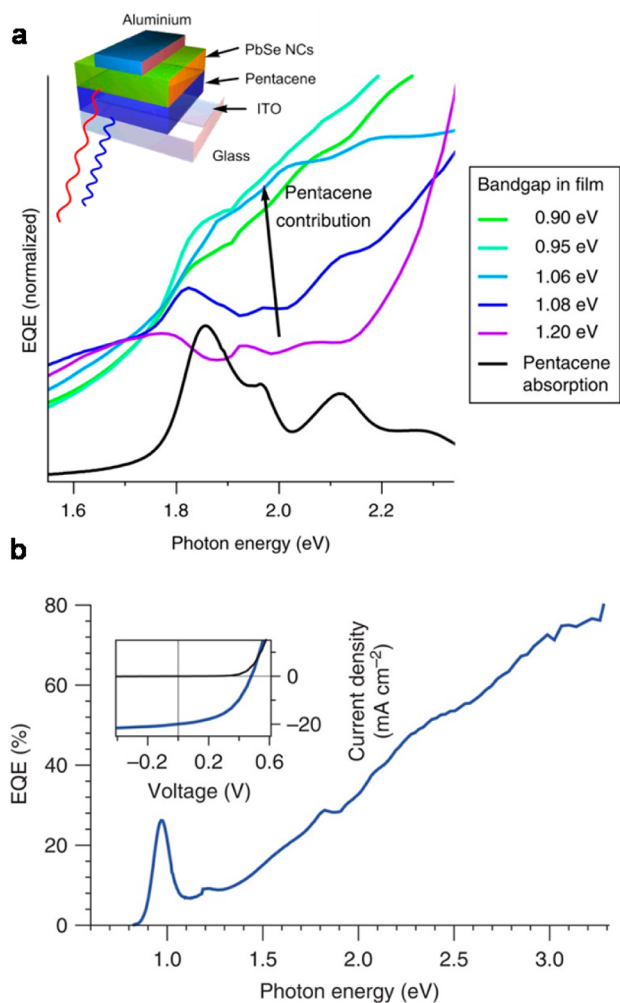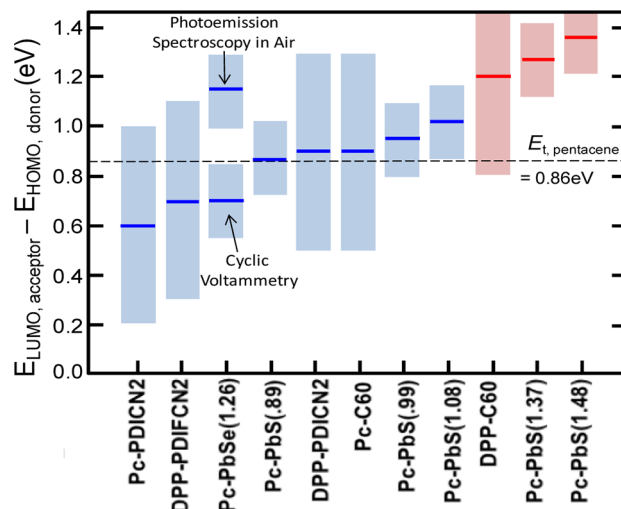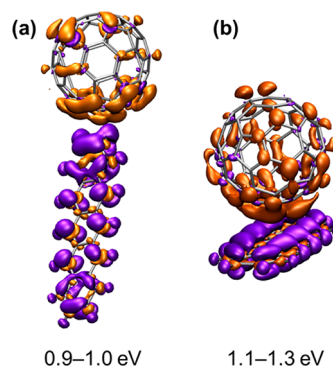

FIGURE 10. (a) Normalized external quantum efficiency spectra of pentacene solar cells prepared with a size series of PbSe NCs. A contribution from pentacene is observed in devices with NCs up to 1.08 eV, indicated with an arrow. The inset shows the device structure studied. (b) EQE of the best PbSe−pentacene device. The inset shows the current−voltage data with a power conversion efficiency of 4.7% under AM 1.5G illumination. The NC bandgap in the film is 0.98 eV. Courtesy of Ehrler et al. Reprinted by permission from ref 5. Copyright 2012 Nature Publishing Group.

FIGURE 12. Calculated charge transfer state energies for pentacene−C_{60} donor−acceptor pairs in (a) head-to-tail and (b) face-to-face configurations. Reprinted from ref 3 with permission from John Wiley and Sons.

state energy was computed to be 0.9−1.0 eV for the head-to-tail geometry, potentially low enough to break up the pentacene triplet state.[3] The face-to-face geometry is predicted to have a CT state energy of 1.1−1.3 eV, not low enough to separate the pentacene triplet.[3] The calculation supports the conclusion that the pentacene triplet and the pentacene/C_{60} CT state are roughly isoenergetic.[3]

Finally, it is important to note that pentacene/C_{60} bilayer solar cells show high EQEs up to ∼70%.[16] Considering that the pentacene triplets are formed almost instantaneously (∼80 fs) after photoexcitation,[11,12,15] such high efficiencies

are hard to explain if the photocurrent is only created by residual pentacene singlet excitons.

4. Singlet-Fission Solar Cells with Additional Low-Energy Donors

Perhaps the first solar cell designed specifically to exploit singlet exciton fission relied on tetracene rather than pentacene.[2] Singlet fission in tetracene has been thought to be an endothermic process,[23] although it has also recently been suggested that the energy barrier for singlet fission in tetracene could be overcome through coherent coupling and entropic gain.[29] Geacintov et al. in the 1960s used photoluminescence, emitted by singlet excitons left after
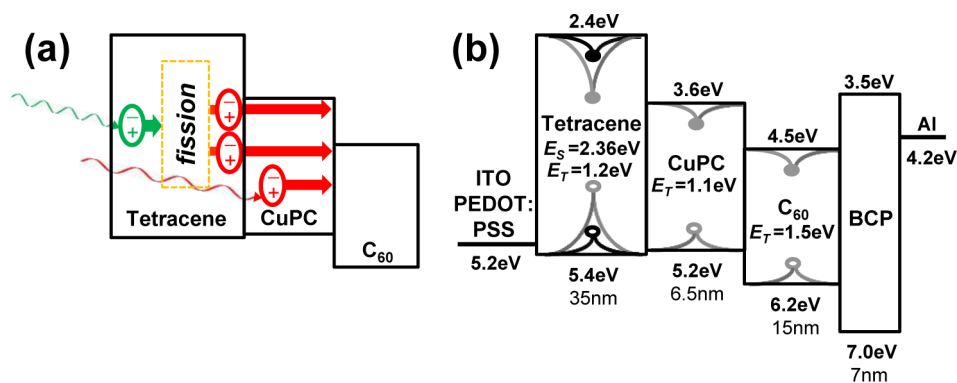
FIGURE 13. (a) A schematic of a solar cell exhibiting singlet fission. Tetracene and CuPC are donors, and C_{60} is an acceptor. Tetracene performs singlet fission, and CuPC absorbs long-wavelength photons. (b) Energy diagram of a tetracene/CuPC photovoltaic cell. Reproduced from ref 2. Copyright 2011 American Chemical Society.

singlet fission, as a method to monitor the efficiency of singlet fission as a function of temperature and found that the energy barrier for singlet fission in tetracene is $2E(T_1) - E(S_1) = 0.16$ eV.[23,30]

Tetracene is considered to have the ideal energetic structure for singlet fission photovoltaics because it absorbs at $\lambda < 550$ nm and produces triplet excitons with energy $E_T = 1.2$ eV, close to the ideal bandgap (~ 1 eV) with maximum efficiency in a single junction solar cell under the SQ limit, see Figure 2.[6] Also, tetracene is known to exhibit long triplet exciton diffusion in its crystalline form.[31]

Chu et al. demonstrated a tetracene/C_{60} solar cell with the power conversion efficiency of 2.3% and short-circuit current of 7.0 mA/cm² under 100 mW/cm² AM 1.5 illumination.[32,33] The device structure was ITO/PEDOT:PSS/tetracene (80 nm)/C_{60} (30 nm)/BCP (8 nm)/Al. However, in order to benefit from tetracene's capability of singlet fission, the photovoltaic cell needs to be combined with a long-wavelength absorber.

Jadhav et al. put tetracene thin films together with a thin layer of copper phthalocyanine (CuPC), which absorbs at $\lambda < 700$ nm, to fill the absorption gap above tetracene's triplet energy and below its singlet energy,[2] as illustrated in Figure 13a. The full device implementation is shown in Figure 13b. In this device, triplet excitons from tetracene diffuse through CuPC and separate into charge at the CuPC/C_{60} interface.[2] Figure 14 shows the external quantum efficiency and current−voltage characteristic of the tetracene/C_{60} devices with and without an insertion of CuPC, demonstrating successful integration of tetracene photovoltaic cells with the low bandgap absorber.

Similar device structures were also reported by Hong et al.[34] and Kinoshita et al.[35] except that tetracene was replaced by pentacene. These heterojunction devices, that

is, pentacene/CuPC or zinc phthalocyanine (ZnPC)/C_{60}, demonstrated enhanced open-circuit voltages and power conversion efficiencies with the insertion of a thin phthalocyanine layer. However, as the distinct peak from pentacene at $\lambda = 670$ nm disappears from the EQE spectra when the phthalocyanine layer is thicker than ~ 5 nm, it appears that the pentacene triplets do not transfer to phthalocyanine. Indeed, the triplet energies of ZnPC and CuPC are around 1.1 eV;[36] therefore, the pentacene triplet ($E_T = 0.86$ eV[10]) cannot move to the phthalocyanine layer. Consequently, these three layer devices do not effectively employ singlet exciton fission.

The trilayer approach of adding a low-energy donor, however, has limitations. It extends the required diffusion distance for triplet excitons, and the triplet energy and the HOMO energy of donors should be properly aligned to ensure the barrier-less exciton and charge transport, limiting the selection of materials. In the next section, we will discuss the simpler bilayer architecture that incorporates low bandgap materials as an acceptor.

5. Singlet–Fission Solar Cells with Low-Energy Acceptors

Similar to tetracene photovoltaic cells, pentacene solar cells need to accompany materials that absorb at wavelengths above 700 nm to improve the product of voltage and current instead of only doubling photocurrents. Jadhav et al.[3] and Ehrler et al.[4,5] reported pentacene singlet fission devices with acceptors of PbSe and PbS colloidal NCs, which can absorb down to 0.7 eV, comparable to the triplet energy of pentacene. As shown in section 3, PbSe NCs are superior to PbS NCs in terms of triplet exciton dissociation, because PbSe NCs have lower ionization potentials and hence provide greater driving force for charge transfer of triplet excitons.
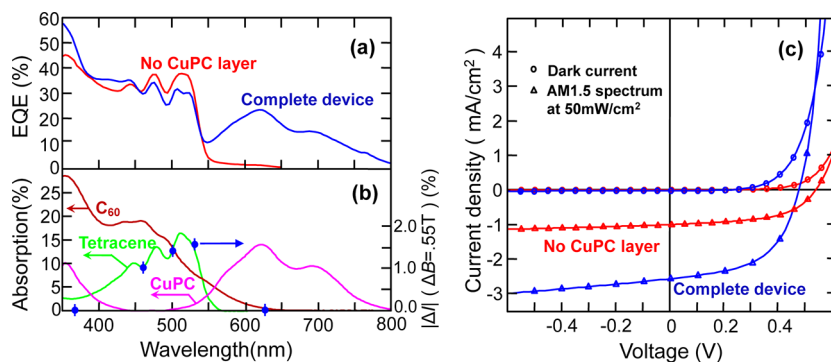
FIGURE 14. (a) External quantum efficiency under short circuit conditions. The blue line is the device depicted in Figure 13, and the red line is the equivalent device without the CuPC layer. (b) Absorption spectra of each layer calculated by optical interference modeling. (c) Current−voltage characteristics for the tetracene−CuPC−C_{60} heterojunction device (blue) and the tetracene−C_{60} device (red). Reproduced from ref 2. Copyright 2011 American Chemical Society.
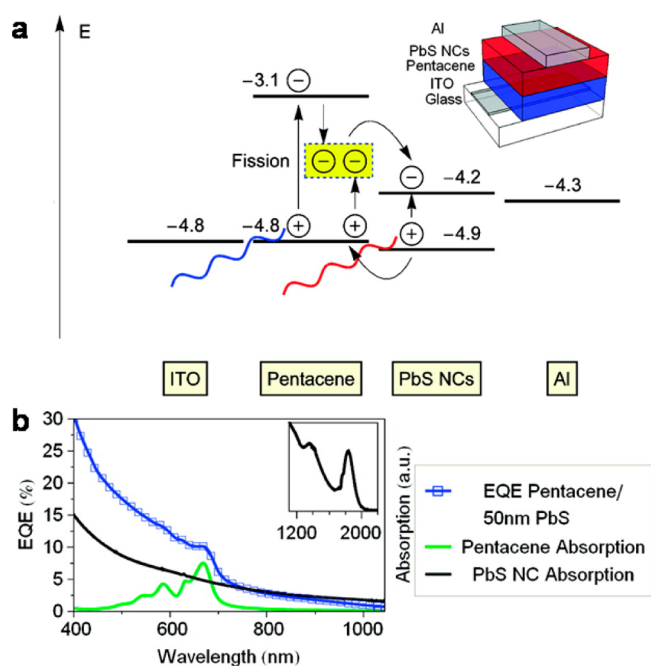

FIGURE 15. (a) Device schematic and energy diagram of pentacene/PbS devices. The pentacene singlets convert to triplets on the 80 fs time scale.[12] These triplets are dissociated at the pentacene/PbS nanocrystal interface. (b) External quantum efficiency of a device with 50 nm layers of both pentacene and PbS nanocrystals (□) in comparison with the absorption of neat pentacene (green) and nanocrystal thin films (black). The inset shows the infrared absorption onset of the nanocrystals. Courtesy of Ehrler et al. Reproduced from ref 4. Copyright 2012 American Chemical Society.

Figure 15a shows the structure of pentacene/PbS NC devices fabricated by Ehrler and co-workers.[4] The EQE spectrum, as shown in Figure 15b, exhibits an absorption peak at $\lambda = 670$ nm, indicating the photocurrent contribution from pentacene. A similar phenomenon was also observed by Jadhav et al. (see Figure 8c).[3] The best device was achieved by adding a 100-nm-thick zinc oxide layer

between the PbS NC layer and the metal contact for better charge extraction, exhibiting a power conversion efficiency of 0.85%.[4]

Ehrler et al. demonstrated pentacene/PbSe NC photovoltaic cells with power conversion efficiencies of 4.7%, see Figure 10b for the EQE and current−voltage characteristics.[5] To minimize the energy loss during both triplet dissociation and hole transfer from NCs to pentacene, the bandgap of NCs was chosen to be as large as possible while maintaining the capability to ionize triplets.[5] Separate studies by Jadhav et al. found that the IQE of pentacene in pentacene/PbSe NC devices was only 35%, lower than the pentacene IQE of 63% observed in pentacene/C_{60} devices, see Figure 8d.[3] This implies that exposure to solvents or contamination during ligand exchange might partially damage the pentacene/NC interface.[3] Otherwise, the efficient triplet ionization and high power conversion efficiency in PbSe NC acceptor devices suggest that adopting nanocrystal acceptors in singlet-fission solar cells is a promising approach.

6. Singlet Exciton Fission Sensitization

Singlet fission molecules, including acenes, often exhibit low absorption coefficients ($<10^5$ cm^{-1}), which limits the efficiency of singlet-fission-based solar cells. To overcome this problem, Reusswig et al. devised a solar cell architecture where a singlet fission sensitizer is inserted between a singlet donor and an acceptor, see Figure 16a for the device operation principle.[37] Excitons created by photon absorption of singlet donors migrate to a singlet fission sensitizer, where the number of excitons doubles. In this device, the process of singlet exciton fission is decoupled from photon absorption, exciton diffusion, and charge transport.[37] This architecture can convert a variety of highly light-absorbing molecules to effective singlet fission materials.[37]
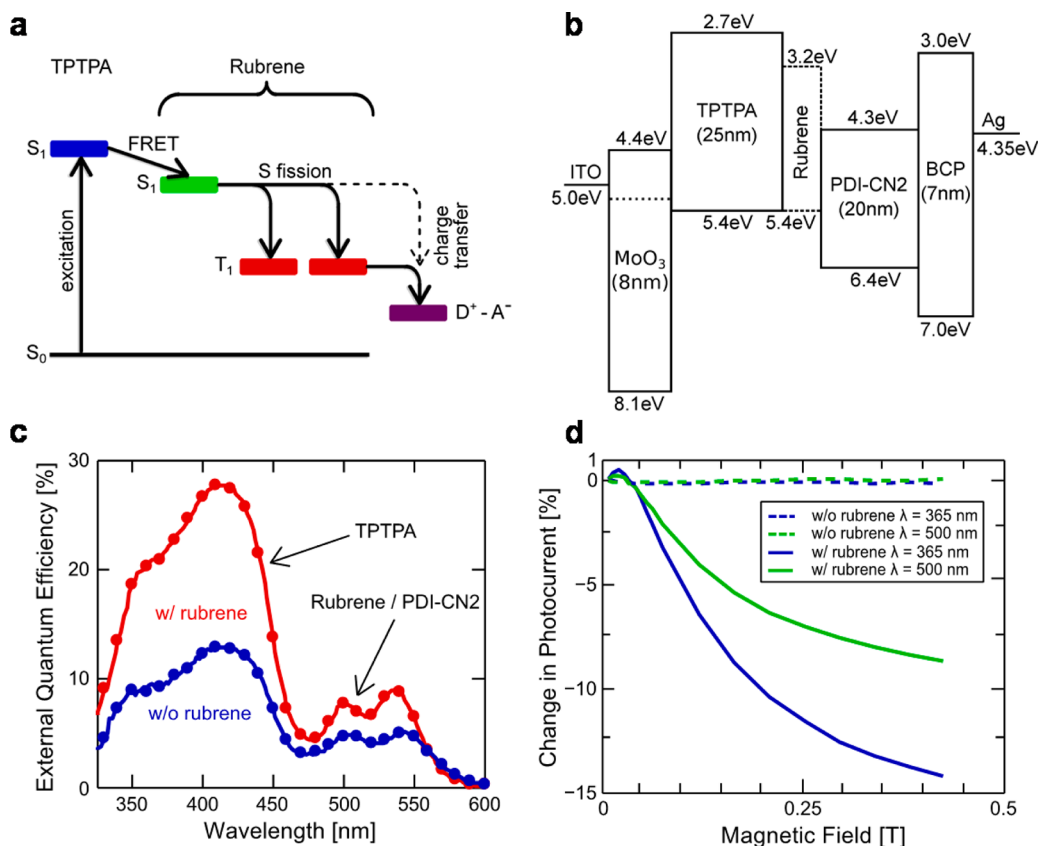
FIGURE 16. (a) Energy flow in photovoltaic devices that exploit a singlet exciton fission sensitizer. Optical excitation populates singlets on TPTPA. The singlet excitons are transferred to rubrene, a singlet fission sensitizer, where they undergo singlet fission, followed by charge transfer at the donor−acceptor interface. (b) A device structure of TPTPA/PDI-CN2 bilayer photovoltaic cells incorporating a singlet fission sensitizer. (c) EQE spectra of the TPTPA/rubrene/PDI-CN2 photovoltaic device compared with the control device. (d) Comparison of magnetic field dependence of photocurrent for TPTPA/PDI-CN2 devices without rubrene (dashed) and with rubrene (solid). The illuminations at $\lambda = 365$ nm (blue) and $\lambda = 500$ nm (green) photoexcite TPTPA and rubrene, respectively. Reprinted with permission from ref 37. Copyright 2012 American Institute of Physics.

Reusswig et al. built a tris[4-(5-phenylthiophen-2-yl)-phenyl]amine (TPTPA)/PDI-CN2 planar heterojunction device with rubrene as the singlet fission sensitizer (see Figure 16b).[37] Figure 16c presents the boost in the efficiency of singlet donor photoexcitations by the singlet fission sensitizer. The EQEs at $\lambda < 450$ nm, where TPTPA absorption dominates, double as a thin layer of rubrene is inserted.

The magnetic field effect on photocurrent confirms that the EQE enhancement owes to energy transfer from TPTPA to rubrene and consequent singlet fission in rubrene; see Figure 16d.[37] The singlet fission sensitizer device shows reduction in photocurrent down to −14% upon photoexcitation of TPTPA under applied magnetic field, meaning that TPTPA absorption undergoes singlet fission. The control device shows almost no magnetic field effect.

7. Conclusion and Outlook

Singlet fission photovoltaics are in their infancy. To achieve high efficiencies, it is necessary to optimize each step in the operation of devices. First, the typically poor optical absorption of singlet fission materials can be overcome by utilizing energy transfer from a good light absorber to singlet fission sensitizers. Second, one of the major loss mechanisms in singlet fission devices is direct dissociation of singlet photoexcitations before undergoing singlet fission. This loss process can be probed using the magnetic field modulation of photocurrent. Finally, to ultimately generate photocurrent, singlet fission donors should be properly matched with acceptors that have LUMOs deep enough to dissociate triplets. Photocurrent spectroscopy and magnetic field probes can be employed to distinguish acceptors that can separate triplets.

Singlet exciton fission doubles photocurrent but halves open-circuit voltages. To increase the net efficiency, singlet fission materials need to be combined with long-wavelength absorbing materials that can capture the photons between the singlet and triplet levels of the singlet fission molecule. We reviewed two device architectures:

singlet-fission photovoltaic cells with low bandgap donors (e.g., tetracene/CuPC/C_{60}) and infrared absorbing acceptors (e.g., pentacene/NCs). At present, the heterojunction of pentacene and PbSe NCs appears to be the most promising system. But these devices presently generate the vast majority of their photocurrent from the NCs. Performance from the singlet fission material is relatively weak. This may be due in part to solution processing the NC film on top of the pentacene layer. An inverted structure may better preserve the properties of pentacene. New organic/inorganic architectures and devices such as pentacene/NC combinations are one among many promising directions for the field.

BIOGRAPHICAL INFORMATION

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FOOTNOTES

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