

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263952070>

Organic Solar Cells beyond One Pair of Donor–Acceptor: Ternary Blends and More

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · MAY 2013

Impact Factor: 7.46 · DOI: 10.1021/jz400723u

CITATIONS

43

READS

39

3 AUTHORS:



Liqiang Yang

University of North Carolina at Chapel Hill

28 PUBLICATIONS 3,386 CITATIONS

SEE PROFILE



Liang Yan

University of North Carolina at Chapel Hill

31 PUBLICATIONS 376 CITATIONS

SEE PROFILE



Wei You

University of North Carolina at Chapel Hill

81 PUBLICATIONS 4,339 CITATIONS

SEE PROFILE

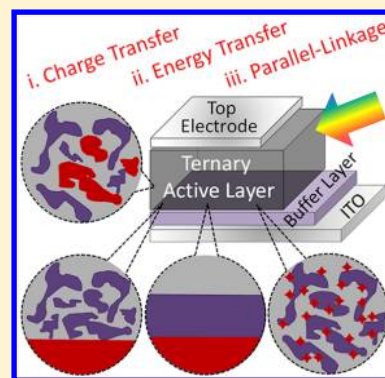
Organic Solar Cells beyond One Pair of Donor–Acceptor: Ternary Blends and More

Liqiang Yang,[†] Liang Yan,[‡] and Wei You^{*,†,‡}

[†]Curriculum in Applied Sciences and Engineering, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3287, United States

[‡]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

ABSTRACT: Ternary solar cells enjoy both an increased light absorption width, and an easy fabrication process associated with their simple structures. Significant progress has been made for such solar cells with demonstrated efficiencies over 7%; however, their fundamental working principles are still under investigation. This Perspective is intended to offer our insights on the three major governing mechanisms in these intriguing ternary solar cells: charge transfer, energy transfer, and parallel-linkage. Through careful analysis of exemplary cases, we summarize the advantages and limitations of these three major mechanisms and suggest future research directions. For example, incorporating additional singlet fission or upconversion materials into the energy transfer dominant ternary solar cells has the potential to break the theoretical efficiency limit in single junction organic solar cells. Clearly, a feedback loop between fundamental understanding and materials selection is in urgent need to accelerate the efficiency improvement of these ternary solar cells.



Organic solar cells typically employ only *two* carbon-based organic semiconductors of distinctly different electronic properties in the “active layer”: a p-type organic semiconductor (i.e., electron-rich or “donor”) for hole transport, and a n-type (i.e., electron-deficient or “acceptor”) for electron transport. These two constitute an organic “p–n” junction: the donor/acceptor interface. With appropriately aligned energy levels, this interface offers enough driving force that excitons, generated by the donor and/or acceptor, can then dissociate into separate charge carriers. After transporting through the active layer, these charge carriers can be harvested by an appropriate cathode and anode pair, completing the light-to-power conversion: the photovoltaic (PV) effect.^{1–8} Remarkably, the power conversion efficiency (PCE) of such a single junction based solar cell, with only *two* components crammed into a ~ 200 nm thick active layer, has rapidly improved from below 1% to over 8% in the past 10 years,^{9,10} mainly driven by significant advances in the design and synthesis of better organic donors, based on increased understanding of structure–property relationships. Unfortunately, these organic donors have an intrinsic narrow absorption width, usually with a full width at half-maximum (fwhm) on the order of 200 nm.¹¹ To exacerbate the ineffective coverage of solar spectrum by these donors, the organic acceptors, dominated by fullerene-based molecules, contribute very little to the light absorption. For these reasons, single junction-based organic solar cells exhibit noticeably poor light-harvesting capability when compared with other types of high efficiency inorganic solar cells; this limits the ultimate efficiency of single junction based organic solar cells to $\sim 15\%$.^{12–15}

To address the issue of poor light-harvesting capability, the best strategy is to identify an acceptor that not only absorbs primarily in the *complementary* region of the solar spectrum to

that of the donor (with an appreciable absorption coefficient, of course), but also maintains the excellent electron accepting and transporting properties of fullerenes. Unfortunately, such an acceptor remains elusive, although progress has been made.¹⁶ Alternatively, one can mix two donor materials of different, ideally complementary, absorption features to maximize the light absorption, together with these successful fullerene derivatives as the acceptor (Figure 1). Furthermore, such a ternary solar cell can still inherit the major advantages of a conventional single junction based solar cell: a simple structure (two electrodes sandwiching the active layer) for an easy

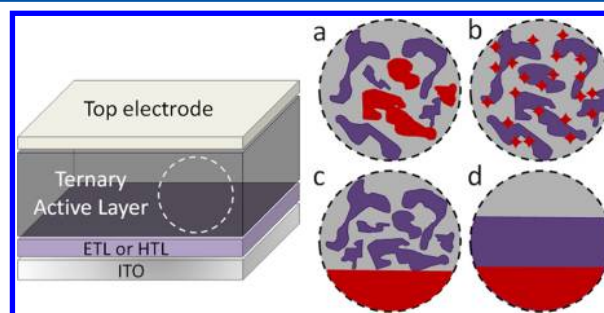


Figure 1. Simple structure ternary solar cells can have various types of active layers: (a) polymer:polymer:acceptor ternary blend, (b) polymer:dye:acceptor ternary blend, (c) polymer:acceptor//small molecule BHJ-bilayer, and (d) acceptor//donor//donor trilayer. (ETL: electron transport layer; HTL: hole transport layer).

Received: April 4, 2013

Accepted: May 9, 2013

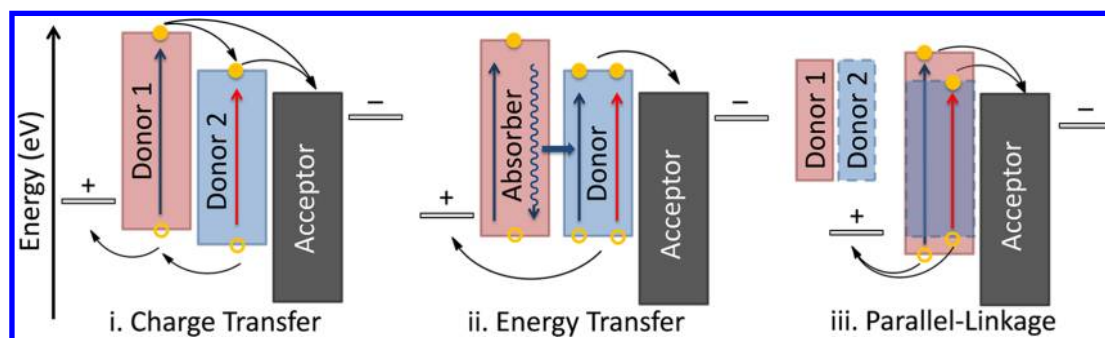


Figure 2. Three fundamentally different mechanisms that can potentially improve the efficiency of ternary organic solar cells: charge transfer, energy transfer, and parallel-linkage.

fabrication process. For these reasons, a growing number of ternary solar cells have been reported.¹⁷ Various compositions of the active layer have been attempted, including two polymer donors blended with a fullerene acceptor,^{18–22} a polymer donor and a small molecule/dye mixed with a fullerene acceptor,^{23–26} bulk heterojunction (BHJ) blend with an additional donor layer underneath,^{27–29} and a trilayer containing two or more donors (Figure 1).^{30,31} In all these reported cases, an increased absorption width of the ternary solar cells has been observed when compared with the corresponding binary systems, which consequently leads to a larger short circuit current density (J_{sc}) for these ternary solar cells than that of the binary systems. However, all these investigations were independently carried out, and the obtained results could be very specific to the reported system. It appears that the design principles responsible for high efficiency in those ternary solar cells have not been carefully summarized. Therefore, in this Perspective, we will focus on the analysis of the fundamental physical principles that govern the photovoltaic process in these ternary systems, based on a few notable recent developments. We hope such a practice will highlight specific principles to guide the future design of ternary systems toward reaching even higher efficiencies.

Figure 2 summarizes three fundamentally different mechanisms, each of which could dominate the photovoltaic processes in these ternary solar cells. In the charge transfer mechanism, both donors can *directly* contribute to the generation of free charge carriers upon interfacing with the acceptor. While electrons can transport through the acceptor domain/network prior to their collection by the cathode, similar to the electrons in the case of binary systems, holes, regardless their origin, all pass through *only one* donor domain before being collected by the anode (e.g., “Donor 1” in the PV process (i) of Figure 2). On the other hand, in the energy transfer mechanism, all holes are *generated* within *only one* donor domain (e.g., “Donor” in the PV process (ii) of Figure 2). The other donor-like component essentially serves only as a light absorber (e.g., “Absorber” in the PV process (ii) of Figure 2), delivering additional photon energy that it absorbs to the donor material via the Dexter or Förster energy transfer. This will generate extra excitons and consequently extra holes in the donor domain (and electrons in the acceptor domain). In general, both the charge transfer and the energy transfer mechanisms require accurate engineering of energy levels and band gaps of all involved materials (including donors, light absorbers, and acceptors), to ensure a successful charge transfer or energy transfer. A third plausible mechanism, the parallel-linkage, which only emerged recently (PV process (iii) in

Figure 2),^{18,32} is significantly different from the aforementioned charge transfer or energy transfer mechanisms. In this special scenario, it is believed that excitons generated in *each* donor domain can migrate to their *respective* donor/acceptor interface and then dissociate into free charge carriers. These generated holes travel through their corresponding donor-linked channels to the anode, while electrons still transport via the acceptor (e.g., fullerene)-enriched domain to the cathode, equivalent to a parallel connection of two individual binary blend-based solar cells.

There are three fundamentally different mechanisms that govern the photovoltaic processes in the ternary solar cells: charge transfer, energy transfer, and parallel-linkage, which are distinctly different from each other. Each of them has its own advantage and limitations.

In the following, we will elaborate on these three fundamentally different mechanisms with selected examples of ternary solar cells. Typically, only one such mechanism dominates the PV process in a given example; however, other mechanisms could also play a role in some cases.

Charge Transfer Dominant Ternary Solar Cell. The ternary blend of polymer:fullerene:dye presents a successful example of improving the light harvesting via the charge transfer mechanism. In such a ternary blend, the additional excitons generated by these dye sensitizers would dissociate at the fullerene interface, and as-generated extra charge carriers (holes) would then transport to the anode via the dominant polymer phase. For example, Ohkita et al. recently reported multicolored dye-sensitized blend solar cells based on quaternary blends of poly(3-hexylthiophene) (P3HT) and phenyl- C_{61} -butyric acid methyl ester (PCBM) with two additional dyes (silicon phthalocyanine bis(trihexylsilyl oxide) (SiPc) and silicon naphthalocyanine bis(trihexylsilyl oxide) (SiNc)).²⁵ These dyes have complementary spectral absorption in the near-IR region where neither P3HT nor PCBM absorbs. When a small amount of these dye molecules are added to the P3HT/PCBM binary blend (10 wt % or less for each dye in regard to P3HT), they are presumably located at the donor/acceptor (i.e., P3HT/PCBM) interface (Figure 3a), driven by the crystallization of both P3HT and PCBM domains. Figure

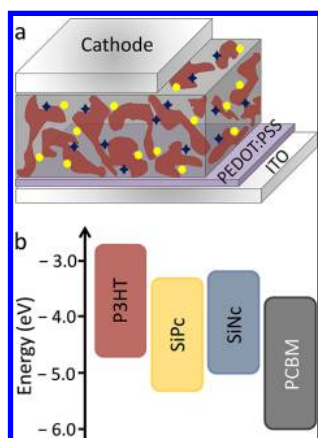


Figure 3. (a) Device configuration of the multicolored dye-sensitized quaternary solar cell, mechanistically following the process (i) of Figure 2. (b) Energy diagram of the four components constituting the active layer in such a quaternary solar cell.

3b shows the energy level alignment of the four organic semiconductors in such a quaternary blend, clearly indicating that the exciton generated from sensitizing these dyes can inject an electron into the PCBM domain and a hole into the P3HT domain. These additional charge generation events lead to two sharp peaks at 670 and 780 nm in the external quantum efficiency (EQE) spectrum, which correspond to the absorption of SiPc and SiNc, respectively. As a result, the quaternary blend solar cells offer ~20% more photocurrent than that of the original P3HT:PCBM binary devices, despite only adding ~13% of such dyes (combined). However, the highest occupied molecular orbital (HOMO) energy cascade that drives hole transfer from dyes to P3HT also leads to a loss of V_{oc} since V_{oc} in such systems is determined by the smallest energy difference between the HOMO levels of those donors and the lowest unoccupied molecular orbital (LUMO) level of the acceptor. Therefore, the V_{oc} of the charge transfer dominant ternary solar cells is basically pinned to the smaller V_{oc} of the corresponding binary blends, which is P3HT:PCBM in this case.

A cascade energy level alignment is required as the charge transfer driving force in the charge-transfer-dominant ternary solar cells.

In addition to these dyes or small molecules,²⁶ polymers can also be used in the ternary solar cells via a charge transfer mechanism. Koppe et al. investigated the effect of adding a narrow band gap polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), into the archetypical P3HT:PCBM binary blend.³³ Due to its narrow band gap, PCPDTBT noticeably extends the spectroscopic response of P3HT:PCBM blends into the near-infrared. More importantly, EQE spectra indicate that these extra PCPDTBT enhance the photosensitivity of the ternary blend, especially in the near-IR region. Since energy levels of P3HT:PCPDTBT:PCBM nicely form a cascade, the dominant mechanism behind such an enhancement is believed to be a charge transfer process. Specifically, the photoinduced charge transfer generates holes on both P3HT and PCPDTBT, and electrons on PCBM. The hole on PCPDTBT is then transferred to P3HT, the dominating

donor that forms the hole transport domain. Interestingly, the efficiency enhancement in such ternary blend devices has only been observed for added amounts of PCPDTBT lower than 20 wt % (vs P3HT+PCPDTBT). This is because for any type of ternary solar cells relying on the charge transfer mechanism (including dyes, small molecules and polymers), only the sensitizers located at the interface between dominating donor (e.g., P3HT) and the acceptor (e.g., PCBM) can generate *additional* photocurrent. Excess sensitizers may function as exciton traps, leading to a drop in fill factor (FF) and adversely impacting the overall efficiency as observed in the P3HT:PCPDTBT:PCBM devices.³³

Such charge transfer mechanism can also occur in BHJ-bilayer ternary solar cells, in addition to complete BHJ-based ones in the previous discussion. For example, Zhu et al. added an additional layer of P3HT:PCBM-based BHJ blend onto a pre-evaporated copper phthalocyanine (CuPc) layer (Figure 4a).²⁷ It is believed that PCBM in the upper P3HT:PCBM

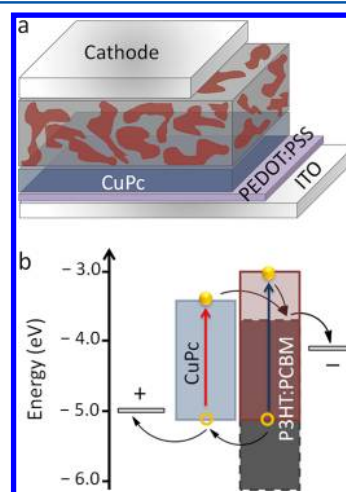


Figure 4. (a) Device structure of BHJ-bilayer ternary solar cells with CuPc and P3HT. (b) Schematic of photocurrent generation with charge transfer at the CuPc/P3HT interface.

based BHJ blend is in contact with the underlying CuPc to form another CuPc//PCBM bilayer subcell. Therefore, excitons generated from both P3HT and CuPc can dissociate at their corresponding donor/PCBM interface, with holes generated in both P3HT and CuPc, and electrons in PCBM. While the electrons can transport via the PCBM domain-linked channels to the cathode, holes from the P3HT domain will travel through the CuPc layer prior to the collection by the anode. This is energetically feasible, since the HOMO level of CuPc is close to that of P3HT. In this special ternary solar cell (BHJ+bilayer), CuPc serves two purposes: it generates *additional* charge carriers as it would in a typical bilayer solar cell, and it also works as the *charge transport* buffer layer for the hole carriers contributed by the P3HT. For these reasons, the charge transport mechanism is the dominating one in these special ternary solar cells.

Energy Transfer Dominant Ternary Solar Cell. The signature difference between the energy transfer mechanism and the charge transfer mechanism is that these additional absorbers do not *directly* generate free charge carriers in the energy transfer dominating ternary solar cells. Instead, these extra absorbers can harvest more sunlight, i.e., serving as the “energy donor”, and transfer these extra photogenerated excited states to the

“energy acceptor” (i.e., “Donor” in the process (ii) of Figure 2). These extra excited states, now on the (primary) donor, can dissociate with acceptors to generate more free charge carriers. Thus, the end result of a ternary solar cell dominated by the energy transfer mechanism is similar to that of the charge transfer based one: a broadened EQE spectrum with an increased J_{sc} .

Two types of energy transfer mechanisms can be applied: long-range, resonance-based Förster energy transfer, and short-range, electron exchange-based Dexter energy transfer. In either case, an important prerequisite is that excitons generated from the additional light absorbing material (“Absorber” in the process (ii) of Figure 2), should not be quenched by the acceptor. In contrast, the charge transfer dominant mechanism would typically require that the energy levels of “Donor 2” (in the process (i) of Figure 2) be in between those of “Donor 1” and the acceptor.

Figure 5 describes one recent example where Yang et al. employed the energy transfer mechanism to improve the light

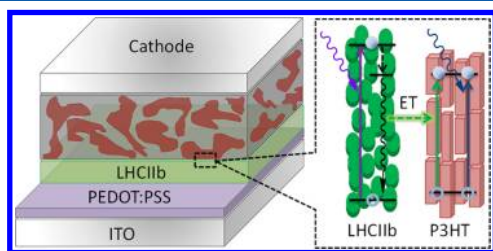


Figure 5. Device structure of an LHCIIb-enhanced bilayer solar cell with the schematic of energy transfer (ET) in the contact area of LHCIIb/P3HT.

absorption and the efficiency of ternary solar cells.²⁸ It should be noted that an almost identical device structure is also presented in Figure 4a. In that case, however, the charge transfer is identified as the dominating mechanism.²⁷ In the current demonstration (Figure 5), a layer of light-harvesting chlorophyll a/b-binding protein of photosystem II (LHCIIb), the most abundant membrane protein on earth, is inserted in between the active layer (P3HT:PCBM) and the anode. Although only a thin layer of LHCIIb (e.g., 40 nm) is used, the extra energy arising at the LHCIIb/P3HT interface leads to a broader optical absorption in this ternary device with an enhanced photocurrent. Supported by the evidence acquired from a number of carefully designed experiments, the authors believe that it is the energy transfer from photons absorbed by LHCIIb to the P3HT that leads to the improved J_{sc} (~30% increase). As a result, the overall efficiency of LHCIIb//P3HT:PCBM device can be improved by 30% when compared with the reference device without the LHCIIb layer. Please note that in the current device configuration (Figure 5), this LHCIIb layer also must act as a hole transport layer between P3HT and the anode, in addition to working as an absorber. However, due to the relatively poor hole mobility of the LHCIIb, the LHCIIb layer cannot be very thick (e.g., optimal thickness ~40 nm), which puts a limit on the absorption enhancement (and thereby the J_{sc} improvement) in the current design. Ideally, in a more general design, absorbers should be able to mix directly into the BHJ structure to avoid the transport limit, while still maintaining their light absorption and energy transfer abilities. In this scenario, further improvement can be expected from the energy transfer mechanism. Such a concept of “energy transfer”

has already been utilized in organic dye sensitized solar cells, where energy relay dyes were dispersed in the electrolyte for a better light absorption of high energy photons. The energy from high energy photons was then transferred to sensitizing dyes through the Förster energy transfer, leading to a 26% increase in PCE.³⁴

As discussed above, both the charge transfer mechanism and the energy transfer mechanism can effectively increase the J_{sc} by broadening the light absorption spectrum and improving the EQE. However, unlike the charge transfer mechanism, the energy transfer, if applied properly (*vide infra*), has the potential to dramatically improve the efficiency of such solar cells, even surpassing the well-known Shockley–Queisser (S-Q) limit.^{35,36} The S-Q limit of single p–n junction cell considers two general loss mechanisms in the photon-to-electricity conversion. The first is the thermalization loss, where photons with a higher energy than band gap will first relax to the band edge prior to the generation of charge carriers. The second—the spectrum loss—states that photons with energy less than the band gap of the light absorbing materials cannot be captured to produce the photoelectrons. Fortunately, there are a number of approaches to exceed the S-Q limit.^{15,37} Below we will briefly discuss two such strategies that are more pertinent to ternary solar cells, especially in conjunction with the energy transfer mechanism.

Singlet fission (SF), referring to the conversion of one singlet exciton of higher energy into two triplet excitons of lower energy, provides a pathway that can reduce the thermalization loss. If engineered properly within a solar cell, SF would improve the internal quantum efficiency by a factor of 2 for the high energy end of the solar spectrum (assuming 100% fission), thereby overcoming the S-Q limit.^{38,39} However, SF with high quantum yields has only been observed in a few organic materials (typically acenes),⁴⁰ and the effectiveness of efficiency enhancement by the direct introduction of an SF material as a donor is being actively debated.^{35,39} For example, the highest power conversion efficiency observed to date is only 4.7%, in a bilayer structure of pentacene and PbSe nanocrystals.⁴¹ Nevertheless, an alternative approach, arguably more effective and practical, is to combine the SF with the energy transfer mechanism in a ternary device. In this scenario, the multiple triplet excitons generated by the SF material can be energy-transferred to the material of a smaller band gap, akin to the energy transfer from the “Absorber” to the “Donor” in the process (ii) of Figure 2. Schematically shown in Figure 6a, Baldo et al. demonstrated one such example where tetracene is selected as the SF material (i.e., the absorber) and CuPc serves as the small band gap donor, respectively.³¹ Both tetracene and CuPc are stacked in a multilayer planar junction, with C₆₀ as the electron acceptor, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as the exciton and hole blocking layer. As illustrated in Figure 6b, the SF process in tetracene can convert one singlet exciton of higher energy into two triplet excitons of lower energy. Since the triplet excitons have long diffusion lengths up to 100 nm, these triplet excitons generated in the tetracene layer of 35 nm can diffuse to the interface of tetracene/CuPc and transfer the energy to the triplet exciton in CuPc through the Dexter mechanism. Subsequently, the triplet excitons in CuPc would further diffuse to the CuPc/C₆₀ interface where these extra excitons dissociate to generate photocurrent. Although the absolute PCE of the solar cell is not very impressive (1.27%), the cell has about 70% SF efficiency. A related observation has been reported previously by Leo et al.,

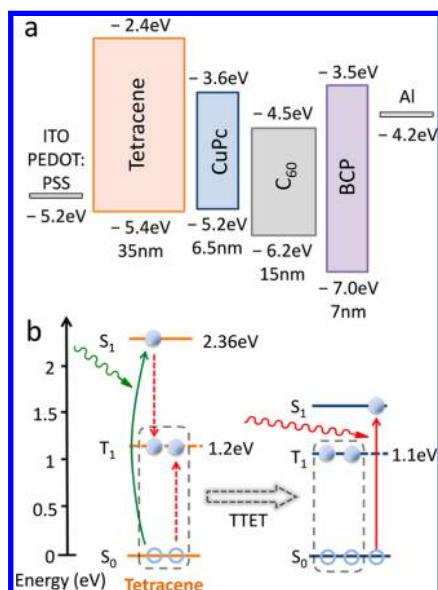


Figure 6. (a) Device structure of the singlet fission enhanced planar heterojunction solar cell with the energy level diagram of all components. (b) Schematic of a photovoltaic exhibiting singlet fission. Solid arrows are optical transition; red dashed arrows are electronics transitions associated with multiple exciton generation. (TTET: triplet–triplet energy transfer).

where multiple heterojunctions of pentacene, zinc phthalocyanine (ZnPc), and C_{60} were investigated.³⁰

Incorporating singlet fission or upconversion materials into the energy transfer dominant ternary solar cells can potentially surpass the theoretical efficiency limit.

Upconversion, on the other the hand, offers an effective means to utilize the photons below the band gap of the primary donor in the solar cell, by converting multiple photons of lower energy (typically near-infrared) to a photon of higher energy (now within the absorption of the primary donor).⁴² Having access to the previously untapped source of NIR photons would therefore lift the S-Q limit. Two different approaches have dominated the research on exploring the upconversion process, namely, spectral conversion by lanthanide ions⁴³ and photon upconversion based on triplet–triplet annihilation (TTA).^{44–47}

In the first approach, typically mixed lanthanide compounds are used to achieve the upconversion,^{43,48} although the method of applying these lanthanides varies. Generally, the upconversion layer is incorporated into the solar cell as an external, “add on” layer.⁴⁹ While this approach offers design convenience (e.g., separating the design of the upconversion layer from the solar cell) and very good transferability among different solar cells platforms (e.g., similarly designed upconversion layers can be used for both inorganic solar cells and organic ones), it does have pitfalls. For example, there would be space-gaps between the add-on upconversion layer and the solar cell, which would noticeably (or even significantly) impact the absorption of these IR photons. Therefore, it would be beneficial to *integrate* the upconversion layer into the already functional solar cells.

One such attempt was reported by Wang et al. recently,⁵⁰ where they doped the hole extraction layer in their organic solar cells, MoO_3 , with rare earth metal ions (Yb, Er). Such a doped MoO_3 layer not only maintains its original role as a hole transport layer, but also has the additional capability of up-converting IR photons. Mechanistically, the Yb^{3+} ion will target photons in the 900–1000 nm range, which are not absorbed by the active layer of P3HT:PCBM in Wang’s study. The Er^{3+} ion will then accept the energy from the excited Yb^{3+} ion, giving rise to up-converted Er^{3+} emission in the range of 500–600 nm, well within the absorption region of the P3HT (Figure 7a).

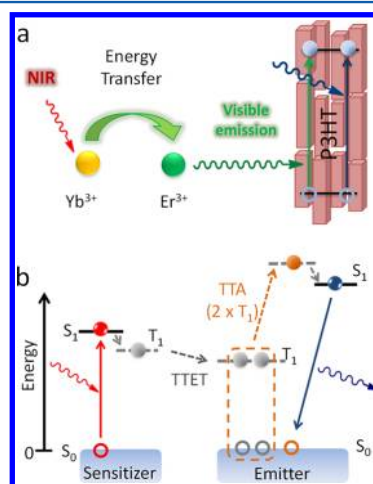


Figure 7. (a) Schematic of photocurrent enhancement in the BHJ device with upconversion phosphors. (b) Schematic of upconversion process in the sensitized TTA system. (TTET: triplet–triplet energy transfer).

Through this tandem process, photons with energy lower than the band gap of P3HT can be utilized. Although the reported improvement of photocurrent from upconversion is less than 1% under 1 sun (AM 1.5G) due to the low efficiency of such upconversion processes, effectively implementing this upconversion process offers a new direction for increasing the efficiency of organic solar cells. For example, Hummelen et al. decorated these upconversion nanoparticles with organic NIR dyes.⁵¹ These antenna dyes can transfer the NIR solar energy to these upconversion nanoparticles via the Förster energy transfer, thereby circumventing the weak and narrow band absorption of these upconversion nanoparticles. According to the authors, this “dye-sensitized upconversion” (DUC) process can dramatically enhance the overall upconversion by a factor of ~3300 compared with the original spectral response of undecorated nanoparticles, representing a significant leap forward in effectively utilizing sub-band gap photons.

The second approach is built upon the TTA, a well-known but less-explored for practical use photophysical process.⁵² In the TTA process, two triplet excitons can form a triplet–triplet pair intermediate state, which can then generate a singlet exciton and a ground state if the energy of the triplet–triplet pair is greater than that of the singlet. An as-generated singlet exciton can further decay to the ground state to give out delayed fluorescence of higher energy than the original triplet exciton. Through this process, TTA converts the low-energy excited state (triplet exciton) to a high-energy excited state (singlet exciton), similar to the spectral conversion by these rare earth metal ions. For a long period of time, TTA had been

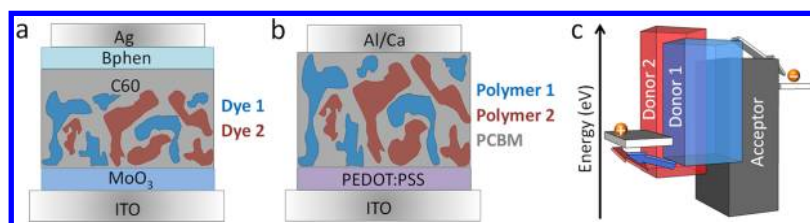


Figure 8. Device structures of a parallel-linkage ternary solar cell based on (a) dye molecules and (b) polymers. (c) Schematic of the photovoltaic in the parallel-linkage ternary device.

limited to a handful of molecules and typically resulted in low efficiency.^{44,45,47} However, in recent years, Castellano et al., among others, discovered that the introduction of metal–organic chromophores as sensitizers into the TTA system can significantly enhance the TTA emission from the emitter.⁴⁶ Schematically shown in Figure 7b, the sensitizer, usually a heavy metal based complex with strong spin orbit coupling, would absorb photons of energy smaller than that of the singlet of the emitter (also an efficient annihilator such as rubrene). Due to the strong spin orbit coupling in the sensitizer, the yield of singlet–triplet intersystem crossing is almost up to 100%,⁵³ leading to a high population of triplet excitons in the sensitizer with energy larger than that of the triplet in the emitter. The triplet–triplet energy transfer would then transfer the energy from the sensitizer to the emitter/annihilator. Subsequently, two triplet excitons in the emitter would annihilate to generate a singlet exciton, which would result in the delayed emission from the emitter. In fact, the quantum efficiency of such a “sensitizing” mechanism-based TTA process can go beyond the theoretic limit of 11.1%.⁵⁴ In practice, the sensitized TTA has been applied in hydrogenated amorphous silicon solar cells to improve the EQE of such solar cells under (48 ± 3) suns (AM1.5) illumination.⁵⁵ For applications in ternary organic solar cells, both the lanthanide-based DUC nanoparticle and the chromophore-sensitized TTA upconversion composite can serve as the “Absorber” in the process (ii) of Figure 2.

Parallel-Linkage Ternary Solar Cell. Unlike the charge transfer or the energy transfer based ternary solar cells where the operating mechanisms have been fairly well understood, a complete and definitive picture of the working mechanism for these “parallel-linkage” ternary solar cells is still under development. The proposed names, “parallel BHJ” and “parallel-like BHJ”, or “PBHJ” in short, were suggested based on experimental observations from two pioneering studies, independently reported by Meerholz and Würthner et al. on small molecules³² and You et al. on conjugated polymers.¹⁸ In the former study, the active layer combines C_{60} as the acceptor and two merocyanine dyes as the double-donors via coevaporation (Figure 8a), whereas the latter study employs two different polymers as the mixed donors and PCBM as the acceptor to form the active layer via spin coating (Figure 8b). Nevertheless, these two studies share a few key findings, based on their carefully planned investigations. First and foremost, the V_{oc} of such PBHJ cells varies according to the composition of the mixed donors, but falls in between those values of “subcells” based on the individual donor:fullerene (a binary blend). Second, the J_{sc} of these PBHJ cells also depends upon the composition of the donors in the active layer. Unlike the V_{oc} of the PBHJ cells, which will never surpass the highest V_{oc} of these individual “subcells”, the highest J_{sc} of these PBHJ cells can reach noticeably higher values than those from individual “subcells”, due to the significantly expanded EQE response

(and a broader absorption) across a range of greater than 400 nm. Both of these findings can be explained by the proposed new mechanism for these ternary solar cells: two “subcells” are *parallel-connected* without any wires, i.e., all components are mixed together into *one* active layer sandwiched between two electrodes. This proposed mechanism was further supported by more experimental data offered by You et al.¹⁸ They fabricated individual “subcells” containing only one donor and PCBM (1:1 weight ratio) with half the thickness of these PBHJ cells that contained two donors and PCBM (0.5:0.5:1, weight ratio). Together, two such “subcells” have the same materials of almost identical quantity as the corresponding PBHJ cell has. If the proposed parallel-linkage were the dominating mechanism, the J_{sc} of the ternary solar cell would be approximately the sum of those from individual “subcells”, while the V_{oc} would be in between. Indeed, both of these predictions were experimentally confirmed.

In the parallel-linkage ternary solar cells, where two “subcells” are presumably parallel-connected without any wires, neither charge transfer nor energy transfer plays an important role.

Figure 8c schematically shows the proposed mechanism for such PBHJ solar cells. The central hypothesis is that these two donors (either small molecules or polymers) form their *individual* donor-rich domains/phases (as they would do in their individual binary blends with the acceptor), while these two domains/phases share the common acceptor-rich phase (fullerenes). It is postulated that each donor still forms an effective heterojunction with the acceptor (i.e., fullerenes) *independently*, to generate the charge carriers upon photoexcitation. Then electrons would transport through the acceptor-enriched domain prior to their collection by the cathode, while the holes generated from *different* donors would mainly travel through their corresponding donor linked pathways to the anode. In this scenario, all free charge carriers generated from the two *different* donors (and the acceptor) can be collected by the same cathode and anode independently, equivalent to a parallel connection of two binary cells. Though this proposed mechanism captures the essence of the PBHJ, the photovoltaic process in any given PBHJ device could be much more complex. For example, in the PBHJ devices studied by You et al.,¹⁸ the internal quantum efficiency (IQE) of their devices in the longer wavelength range, where only the donor of smaller band gap contributes to the current, has been found to be significantly higher than that of the corresponding “subcells” based on the smaller band gap donors. One plausible

explanation is that the larger band gap donor polymer with a high mobility serves as additional charge transport channel for the charges generated by the smaller band gap donor polymer of a lower mobility. This plausible charge transfer process clearly indicates that other mechanisms can certainly be involved in parallel-linkage ternary solar cells.

Similar observations have also been reported for other ternary systems, including mixed polymers:PCBM ternary blends,^{20,22} a polymer:inorganic:PCBM hybrid blend,⁵⁶ and even in a multiple acceptors system.^{57,58} Therefore, the proposed parallel-linkage mechanism might play a dominant role in these systems as well, implying that this mechanism, although only discovered recently and still missing a clear explanation, might be one of these general operating principles for ternary solar cells. However, more recently, Street et al. proposed another model to explain the observed tunable V_{oc} in these ternary solar cells.⁵⁸ In their suggested alloy model, two electronically similar components in a ternary blend, either two donors or two acceptors, form an electronic alloy with HOMO and LUMO energies based on the average composition of these two components. As a result, the V_{oc} observed varies as the composition of donors or acceptors changes, while the J_{sc} can be increased if suitably paired donors with complementary absorption are used. Therefore, further investigation on these intriguing ternary systems of tunable V_{oc} is certainly required to verify these proposed models, i.e., parallel-linkage and electronic alloy. It is also possible that other models will emerge during further investigation.

Summary and Outlook. From the above discussion, it should become quite clear that these three major mechanisms that govern the photovoltaic process in ternary solar cells—charge transfer, energy transfer, and parallel-linkage—are distinctly different from each other. More importantly, each of them has its own advantages and limitations. In charge transfer dominant photovoltaic devices, a cascade energy level alignment is necessary to prevent the possible energy transfer among components in the BHJ blend, and to ensure efficient exciton splitting and charge transport to the correct electrodes. All of these require accurate energy level matching for all constituents in the solar cells. In addition, the V_{oc} of these ternary solar cells are essentially pinned to the smaller V_{oc} of the corresponding binary blends.^{25,26,33,58} On the other hand, the energy of the excited states (singlet or triplet) is much more important for the energy transfer based ternary solar cells: the additional excitons generated by the absorber cannot be quenched by the acceptor in the same active layer, prior to these excitons being funneled into the donor via energy transfer. For the parallel-linkage ternary solar cells, the mechanism of parallel-linkage still lacks a clear explanation. The formation of independent charge transport channels appears to be critically important in some cases, which requires appropriate phase separation of all components in the blend. However, the formation of electronic alloy may be another approach to the parallel-linkage, implying intimate and uniform electronic interaction between two components. Future developments on these ternary solar cells rely on fostering further a fundamental understanding of these arbitrarily termed mechanisms in representative devices (esp. in successfully demonstrated prototypes), which can facilitate the selection of materials combinations. Such a feedback loop between fundamental understanding and materials selection will certainly accelerate the efficiency improvement of these ternary solar cells, with real potential to break the theoretical efficiency limit in single junction organic solar cells.

A feedback loop between fundamental understanding of these arbitrarily termed mechanisms and materials selection will accelerate the efficiency improvement of these ternary solar cells.

Before we conclude, we intend to identify a few worthy future directions for these ternary solar cells, which can be readily expressed as questions. (a) In the *charge transfer* dominant devices, only one donor forms the charge transport matrix. Is incorporating donor materials of high mobility (i.e., inorganics) as a charge transport matrix with other donors of complementary absorption features to further enhance J_{sc} and FF feasible? (b) For the *energy transfer* dominant devices, incorporating SF materials or upconversion materials as the absorber can theoretically breach the S-Q limit of single junction solar cells; however, little progress has been made on this front.⁵⁹ This is because in all reported prototypes, these SF and upconversion materials also function as the hole transport layer, resulting in low SF and upconversion efficiencies and limited energy transfer. Can we design new methods to disperse SF materials or upconversion materials into BHJ structure rather than using them as an additional/add-on layer? Such a design would likely ensure efficient SF and upconversion and energy transfer from absorbers to donors. (c) In *parallel-linkage* based devices, neither charge transfer nor energy transfer plays an important role. However, appropriate energy level alignment in parallel-linkage devices can facilitate charge transfer or even energy transfer between multiple donors, which, if engineered properly, can enhance exciton generation, charge splitting, and charge transport in parallel-linkage-based devices. How can we utilize charge transfer and/or energy transfer to further improve the efficiency of parallel-linkage-based devices? In fact, it is very likely that the “winning” ternary solar cell, defined by its record-high efficiency, will combine two or all of these mechanisms to maximize all possible benefits while minimizing these limitations.

Finally, we do want to remind the readers that the tandem cell, as a proven successful strategy to significantly enhance the efficiency of any solar cell, remains the most effective approach to harvesting the solar energy, and is likely the leading means of improving efficiency. For example, the highest reported efficiency numbers for organic solar cells, 10.6% for polymer-based devices,⁶⁰ and 12% for the one based on small molecules,⁶¹ both are achieved with the tandem design. Nevertheless, we also want to assure the researchers working on the ternary solar cells that further improvements on these cells are still very much warranted for a number of reasons. For example, these simple structure ternary solar cells are much easier to fabricate than multilayer tandem cells; the associated lower cost of these ternary solar cells can certainly compensate their slightly lower efficiency. Furthermore, these simple structure ternary solar cells can be easily adopted as subcells in the tandem design, thereby further enhancing the energy conversion efficiency—the ultimate goal of research activities on solar cells.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wyou@unc.edu.

Notes

The authors declare no competing financial interest.

Biographies

Liqiang Yang received his B.S. degree in Materials Science and Engineering at Xi'an Jiaotong University in 2004 and obtained an M.S. degree in Materials Engineering at the University of Wisconsin–Milwaukee in 2007. He recently received his Ph.D. degree in Materials Science at the University of North Carolina at Chapel Hill under the direction of Prof. Wei You (2012). After graduation, he stayed in Prof. Wei You's group as a Postdoctoral Research Associate. His current research focus is the development of novel device structures and understanding the structure–properties relationships of novel polymers for organic solar cells.

Liang Yan received his B.S. degree in Polymer Science and Engineering at Tsinghua University, Beijing China, in 2003 and he obtained an M.S. degree in Material Science at Tsinghua University, Beijing, in 2006. Liang then went to the University of Tennessee and obtained his Ph.D. degree under the direction of Prof. Bin Hu in Material Science and Engineering in August 2011. After that he joined Prof. Wei You's group at University of North Carolina at Chapel Hill as a Postdoctoral Research Associate. His research interests include organic photovoltaic and organic/inorganic hybrid solar cell and organic spintronics.

Wei You was born in a small village outside of Chuzhou in the Anhui Province of China, and grew up in Hefei, the provincial capital of Anhui. After receiving a B.S. degree in Polymer Chemistry from the University of Science and Technology of China in 1999, he joined the graduate program of chemistry at the University of Chicago, where he obtained his Ph.D. in 2004 under the guidance of Professor Luping Yu. He then moved west and finished his postdoctoral training at Stanford University in 2006 with Professor Zhenan Bao. In July 2006, he joined the University of North Carolina at Chapel Hill as an Assistant Professor in Chemistry, and was promoted to the rank of Associate Professor in July 2012. Professor You's research interests focus on the development of novel multifunctional materials for a variety of applications, including organic solar cells, molecular electronics, and spintronics. <http://www.chem.unc.edu/people/faculty/you/>

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research (Grant No. N000140911016, and N000141110235), a NSF CAREER Award (DMR-0954280), and a NSF SOLAR Grant (DMR-1125803). W.Y. is a Camille Dreyfus Teacher-Scholar.

REFERENCES

- (1) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor–Acceptor Heterojunctions. *Science* **1995**, *270*, 1789–1791.
- (2) Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromherz, T.; Hummelen, J. C. 2.5% Efficient Organic Plastic Solar Cells. *Appl. Phys. Lett.* **2001**, *78*, 841–843.
- (3) Brabec, C. J.; Shaheen, S. E.; Winder, C.; Sariciftci, N. S.; Denk, P. Effect of LiF/Metal Electrodes on the Performance of Plastic Solar Cells. *Appl. Phys. Lett.* **2002**, *80*, 1288–1290.
- (4) Ma, W. L.; Yang, C. Y.; Gong, X.; Lee, K.; Heeger, A. J. Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv. Funct. Mater.* **2005**, *15*, 1617–1622.
- (5) Li, G.; Shrotriya, V.; Huang, J. S.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. High-Efficiency Solution Processable Polymer Photovoltaic Cells by Self-Organization of Polymer Blends. *Nat. Mater.* **2005**, *4*, 864–868.
- (6) Zhou, H.; Yang, L.; Price, S. C.; Knight, K. J.; You, W. Enhanced Photovoltaic Performance of Low-Bandgap Polymers with Deep LUMO Levels. *Angew. Chem., Int. Ed.* **2010**, *49*, 7992–7995.
- (7) Zhou, H.; Yang, L.; Stuart, A. C.; Price, S. C.; Liu, S.; You, W. Development of Fluorinated Benzothiadiazole as a Structural Unit for a Polymer Solar Cell of 7% Efficiency. *Angew. Chem., Int. Ed.* **2011**, *50*, 2995–2998.
- (8) Price, S. C.; Stuart, A. C.; Yang, L.; Zhou, H.; You, W. Fluorine Substituted Conjugated Polymer of Medium Band Gap Yields 7% Efficiency in Polymer–Fullerene Solar Cells. *J. Am. Chem. Soc.* **2011**, *133*, 4625–4631.
- (9) Service, R. F. Outlook Brightens for Plastic Solar Cells. *Science* **2011**, *332*, 293.
- (10) Zhou, H.; Yang, L.; You, W. Rational Design of High Performance Conjugated Polymers for Organic Solar Cells. *Macromolecules* **2012**, *45*, 607–632.
- (11) Beaujuge, P. M.; Amb, C. M.; Reynolds, J. R. Spectral Engineering in π -Conjugated Polymers with Intramolecular Donor–Acceptor Interactions. *Acc. Chem. Res.* **2010**, *43*, 1396–1407.
- (12) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10% Energy-Conversion Efficiency. *Adv. Mater.* **2006**, *18*, 789–794.
- (13) Kotlarski, J. D.; Blom, P. W. M. Ultimate Performance of Polymer:Fullerene Bulk Heterojunction Tandem Solar Cells. *Appl. Phys. Lett.* **2011**, *98*, 053301–3.
- (14) Nayak, P. K.; Garcia-Belmonte, G.; Kahn, A.; Bisquert, J.; Cahen, D. Photovoltaic Efficiency Limits and Material Disorder. *Energy Environ. Sci.* **2012**, *5*, 6022–6039.
- (15) Lunt, R. R.; Osedach, T. P.; Brown, P. R.; Rowehl, J. A.; Bulović, V. Practical Roadmap and Limits to Nanostructured Photovoltaics. *Adv. Mater.* **2011**, *23*, 5712–5727.
- (16) Sonar, P.; Fong Lim, J. P.; Chan, K. L. Organic Non-fullerene Acceptors for Organic Photovoltaics. *Energy Environ. Sci.* **2011**, *4*, 1558–1574.
- (17) Chen, Y.-C.; Hsu, C.-Y.; Lin, R. Y.-Y.; Ho, K.-C.; Lin, J. T. Materials for the Active Layer of Organic Photovoltaics: Ternary Solar Cell Approach. *ChemSusChem* **2013**, *6*, 20–35.
- (18) Yang, L.; Zhou, H.; Price, S. C.; You, W. Parallel-like Bulk Heterojunction Polymer Solar Cells. *J. Am. Chem. Soc.* **2012**, *134*, 5432–5435.
- (19) Campoy-Quiles, M.; Kanai, Y.; El-Basaty, A.; Sakai, H.; Murata, H. Ternary Mixing: A Simple Method to Tailor the Morphology of Organic Solar Cells. *Org. Electron.* **2009**, *10*, 1120–1132.
- (20) Khlyabich, P. P.; Burkhart, B.; Thompson, B. C. Compositional Dependence of the Open-Circuit Voltage in Ternary Blend Bulk Heterojunction Solar Cells based on Two Donor Polymers. *J. Am. Chem. Soc.* **2012**, *134*, 9074–9077.
- (21) Youngkyoo, K.; Minjung, S.; Hwajeong, K.; Youri, H.; Chang-Sik, H. Influence of Electron-Donating Polymer Addition on the Performance of Polymer Solar Cells. *J. Phys. D: Appl. Phys.* **2008**, *41*, 225101–5.
- (22) Ameri, T.; Min, J.; Li, N.; Machui, F.; Baran, D.; Forster, M.; Schottler, K. J.; Dolfen, D.; Scherf, U.; Brabec, C. J. Performance Enhancement of the P3HT/PCBM Solar Cells through NIR Sensitization Using a Small-Bandgap Polymer. *Adv. Energy Mater.* **2012**, *2*, 1198–1202.
- (23) Suresh, P.; Balraju, P.; Sharma, G. D.; Mikroyannidis, J. A.; Stylianakis, M. M. Effect of the Incorporation of a Low-Band-Gap Small Molecule in a Conjugated Vinylene Copolymer: PCBM Blend for Organic Photovoltaic Devices. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1370–1374.
- (24) Honda, S.; Nogami, T.; Ohkita, H.; Bente, H.; Ito, S. Improvement of the Light-Harvesting Efficiency in Polymer/Fullerene Bulk Heterojunction Solar Cells by Interfacial Dye Modification. *ACS Appl. Mater. Interfaces* **2009**, *1*, 804–810.
- (25) Honda, S.; Ohkita, H.; Bente, H.; Ito, S. Multi-colored Dye Sensitization of Polymer/Fullerene Bulk Heterojunction Solar Cells. *Chem. Commun.* **2010**, *46*, 6596–6598.

- (26) Sharma, G. D.; Singh, S. P.; Roy, M. S.; Mikroyannidis, J. A. Solution Processed Bulk Heterojunction Polymer Solar Cells with Low Band Gap DPP-CN Small Molecule Sensitizer. *Org. Electron.* **2012**, *13*, 1756–1762.
- (27) Zhang, C.; Tong, S. W.; Jiang, C.; Kang, E. T.; Chan, D. S.; Zhu, C. Simple Tandem Organic Photovoltaic Cells for Improved Energy Conversion Efficiency. *Appl. Phys. Lett.* **2008**, *92*, 083310–3.
- (28) Yao, K.; Liu, C.; Chen, Y.; Chen, L.; Li, F.; Liu, K.; Sun, R.; Wang, P.; Yang, C. Integration of Light-Harvesting Complexes into the Polymer Bulk Heterojunction P3HT/PCBM Device for Efficient Photovoltaic Cells. *J. Mater. Chem.* **2012**, *22*, 7342–7349.
- (29) Yuen, A. P.; Hor, A.-M.; Preston, J. S.; Klenkler, R.; Bamsey, N. M.; Loutfy, R. O. A Simple Parallel Tandem Organic Solar Cell based on Metallophthalocyanines. *Appl. Phys. Lett.* **2011**, *98*, 173301–3.
- (30) Hong, Z. R.; Lessmann, R.; Maennig, B.; Huang, Q.; Harada, K.; Riede, M.; Leo, K. Antenna Effects and Improved Efficiency in Multiple Heterojunction Photovoltaic Cells based on Pentacene, Zinc Phthalocyanine, and C₆₀. *J. Appl. Phys.* **2009**, *106*, 064511–6.
- (31) Jadhav, P. J.; Mohanty, A.; Sussman, J.; Lee, J.; Baldo, M. A. Singlet Exciton Fission in Nanostructured Organic Solar Cells. *Nano Lett.* **2011**, *11*, 1495–1498.
- (32) Ojala, A.; Bürckstümmer, H.; Stolte, M.; Sens, R.; Reichelt, H.; Erk, P.; Hwang, J.; Hertel, D.; Meerholz, K.; Würthner, F. Parallel Bulk-Heterojunction Solar Cell by Electrostatically Driven Phase Separation. *Adv. Mater.* **2011**, *23*, 5398–5403.
- (33) Koppe, M.; Egelhaaf, H.-J.; Dennler, G.; Scharber, M. C.; Brabec, C. J.; Schilinsky, P.; Hoth, C. N. Near IR Sensitization of Organic Bulk Heterojunction Solar Cells: Towards Optimization of the Spectral Response of Organic Solar Cells. *Adv. Funct. Mater.* **2010**, *20*, 338–346.
- (34) Hardin, B. E.; Hoke, E. T.; Armstrong, P. B.; Yum, J.-H.; Comte, P.; Torres, T.; Frechet, J. M. J.; Nazeeruddin, M. K.; Gratzel, M.; McGehee, M. D. Increased Light Harvesting in Dye-Sensitized Solar Cells with Energy Relay Dyes. *Nat. Photonics* **2009**, *3*, 406–411.
- (35) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p–n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32*, 510–519.
- (36) Giebink, N. C.; Wiederrecht, G. P.; Wasielewski, M. R.; Forrest, S. R. Thermodynamic Efficiency Limit of Excitonic Solar Cells. *Phys. Rev. B* **2011**, *83*, 195326–6.
- (37) Semonin, O. E.; Luther, J. M.; Choi, S.; Chen, H.-Y.; Gao, J.; Nozik, A. J.; Beard, M. C. Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell. *Science* **2011**, *334*, 1530–1533.
- (38) Hanna, M. C.; Nozik, A. J. Solar Conversion Efficiency of Photovoltaic and Photoelectrolysis Cells with Carrier Multiplication Absorbers. *J. Appl. Phys.* **2006**, *100*, 074510–8.
- (39) Nozik, A. J. Nanoscience and Nanostructures for Photovoltaics and Solar Fuels. *Nano Lett.* **2010**, *10*, 2735–2741.
- (40) Smith, M. B.; Michl, J. Singlet Fission. *Chem. Rev.* **2010**, *110*, 6891–6936.
- (41) Ehrler, B.; Walker, B. J.; Böhm, M. L.; Wilson, M. W. B.; Vaynzof, Y.; Friend, R. H.; Greenham, N. C. Situ Measurement of Exciton Energy in Hybrid Singlet-Fission Solar Cells. *Nat. Commun.* **2012**, *3*, 1019–6.
- (42) Conibeer, G. Third-Generation Photovoltaics. *Mater. Today* **2007**, *10*, 42–50.
- (43) van der Ende, B. M.; Aarts, L.; Meijerink, A. Lanthanide Ions as Spectral Converters for Solar Cells. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11081–11095.
- (44) Parker, C. A.; Hatchard, C. G. Sensitized Anti-Stokes Delayed Fluorescence. *Proc. Chem. Soc.* **1962**, 386–387.
- (45) Parker, C. A.; Joyce, T. A. Phosphorescence of Benzophenone in Fluid Solution. *Chem. Commun. (London)* **1968**, 749–750.
- (46) Singh-Rachford, T. N.; Castellano, F. N. Photon Upconversion Based on Sensitized Triplet–Triplet Annihilation. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.
- (47) Zhao, J.; Ji, S.; Guo, H. Triplet–Triplet Annihilation based Upconversion: From Triplet Sensitizers and Triplet Acceptors to Upconversion Quantum Yields. *RSC Adv.* **2011**, *1*, 937–950.
- (48) Haase, M.; Schäfer, H. Upconverting Nanoparticles. *Angew. Chem., Int. Ed.* **2011**, *50*, S808–S829.
- (49) Adikaari, A. A. D.; Etchart, I.; Guering, P.-H.; Berard, M.; Silva, S. R. P.; Cheetham, A. K.; Curry, R. J. Near Infrared Up-Conversion in Organic Photovoltaic Devices using an Efficient Yb³⁺:Ho³⁺ Co-Doped Ln₂BaZnO₅ (Ln = Y, Gd) Phosphor. *J. Appl. Phys.* **2012**, *111*, 094502–7.
- (50) Wang, H.-Q.; Stubhan, T.; Osvet, A.; Litzov, I.; Brabec, C. J. Up-Conversion Semiconducting MoO₃:Yb/Er Nanocomposites as Buffer Layer in Organic Solar Cells. *Sol. Energy Mater. Sol. Cells* **2012**, *105*, 196–201.
- (51) Zou, W.; Visser, C.; Maduro, J. A.; Pshenichnikov, M. S.; Hummelen, J. C. Broadband Dye-Sensitized Upconversion of Near-Infrared Light. *Nat. Photonics* **2012**, *6*, S60–S64.
- (52) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Principles of Molecular Photochemistry: An Introduction*; University Science Books: Sausalito, CA, 2009.
- (53) Wang, X.-y.; Del Guerso, A.; Schmehl, R. H. Photophysical Behavior of Transition Metal Complexes Having Interacting Ligand Localized and Metal-to-Ligand Charge Transfer States. *J. Photochem. Photobiol. C* **2004**, *5*, 55–77.
- (54) Cheng, Y. Y.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. On the Efficiency Limit of Triplet–Triplet Annihilation for Photochemical Upconversion. *Phys. Chem. Chem. Phys.* **2010**, *12*, 66–71.
- (55) Cheng, Y. Y.; Fückel, B.; MacQueen, R. W.; Khoury, T.; Clady, R. G. C. R.; Schulze, T. F.; Ekins-Daukes, N. J.; Crossley, M. J.; Stannowski, B.; Lips, K.; Schmidt, T. W. Improving the Light-Harvesting of Amorphous Silicon Solar Cells with Photochemical Upconversion. *Energy Environ. Sci.* **2012**, *5*, 6953–6959.
- (56) de Freitas, J. N.; Grova, I. R.; Akcelrud, L. C.; Arici, E.; Sariciftci, N. S.; Nogueira, A. F. The Effects of CdSe Incorporation into Bulk Heterojunction Solar Cells. *J. Mater. Chem.* **2010**, *20*, 4845–4853.
- (57) Khlyabich, P. P.; Burkhart, B.; Thompson, B. C. Efficient Ternary Blend Bulk Heterojunction Solar Cells with Tunable Open-Circuit Voltage. *J. Am. Chem. Soc.* **2011**, *133*, 14534–14537.
- (58) Street, R. A.; Davies, D.; Khlyabich, P. P.; Burkhart, B.; Thompson, B. C. Origin of the Tunable Open Circuit Voltage in Ternary Blend Organic Solar Cells. *J. Am. Chem. Soc.* **2013**, *135*, 986–989.
- (59) Congreve, D. N.; Lee, J.; Thompson, N. J.; Hontz, E.; Yost, S. R.; Reuswig, P. D.; Bahlke, M. E.; Reineke, S.; Van Voorhis, T.; Baldo, M. A. External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission–Based Organic Photovoltaic Cell. *Science* **2013**, *340*, 334–337.
- (60) You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C.-C.; Gao, J.; Li, G.; Yang, Y. A Polymer Tandem Solar Cell with 10.6% Power Conversion Efficiency. *Nat. Commun.* **2013**, *4*, 1446–10.
- (61) Heliotech Achieves 12% Organic Solar Cell Efficiency. <http://optics.org/news/4/1/36>.