Organic Semiconductors and Their Application in Energy Harvesting

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ABSTRACT

Over the past several decades, research in organic semiconductors has progressed steadily to the point that commercial applications have been realized in areas such as organic light emitting diodes (OLEDs) for solid state lighting and displays, as well as organic field effect transistors (OFETs) for RFIDs, e-paper and flexible electronics. The use of organic semiconductors for photo-voltaics (PV) has also seen tremendous progress over the past decade with power conversion efficiencies that have risen from 1% to above 10% as reported recently. The urgency for developing low-cost, high-efficiency renewable energy sources is very pressing since worldwide demand for energy is expected to triple by the end of the century. Organic PV provides advantages in its very low-cost manufacturing processes that utilize room temperature techniques, unlike crystalline Si and other inorganic PV technologies that are not cost-effective. Other advantages of OPV includes the use of environmentally friendly materials, and compatibility with roll-to-roll processing for the realization of solar cells in a flexible and conformable platform.

1. INTRODUCTION

Organic semiconductors offer advantages of low material cost, low temperature processes and the ability to engineer materials properties through chemical synthesis which has enabled a large number of potential applications for organic semiconductors in electronics and optoelectronics over the past several decades. Their compatibility with flexible substrates has created prospects for organic semiconductors to be spin coated onto light weight flexible substrates using high-throughput, low-cost roll-to-roll processing. Tremendous progress has been made in recent years that has enabled organic semiconductors to serve as effective light emitters in organic light emitting diodes (OLEDs),[1] logic and memory elements using organic field effect transistors (OFETs),[2] as well as photodetectors. As an example, in Fig. 1a, an OFET is shown (left), where source-drain currents are modulated in the organic semiconductor through the application of a gate voltage. Such devices have applications in flexible electronics (right) or for e-paper and smart textiles. In the OLED device architecture, applying a voltage between the transparent anode and metallic cathode injects charge carriers from both electrodes within the organic semiconductor in the trilayer structure. These injected electrons and holes then create excitons which then emit light upon recombination at a wavelength that is determined by the choice of the active layer. The tremendous success in OLEDs has enabled commercial products from such devices in ultra-thin, full color, flat panel displays, as well as for solid state lighting.

While tremendous progress has been made in organic semiconductors for OFETS and OLEDs, another potential application of organic semiconductors is in converting sunlight to electricity for photo-voltaics (PV).[3,4,5,6] The working principle of such a device is outlined in Fig. 2 where a photon from incoming light is absorbed and results in the formation of electron-hole pairs that generate bound excitons

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in the organic active layer. These excitons are then separated and collected as charges at the terminals, where they generate a photocurrent.[7] This is in contrast to an inorganic semiconductor,[8] where the absorption of a photon leads directly to the creation of free electrons and holes which are then driven away to the respective electrodes through the built-in potential. As with organic semiconductors, the advantage of organic PV lies in the very low-cost manufacturing process utilizing room temperature techniques. In current generation organic solar cells, the composite active layer can be prepared on large area substrates using techniques such as spin-coating, inkjet-printing, spray coating, gravure-coating, which are also compatible with roll-to-roll processing as shown in Fig 2b.[9]

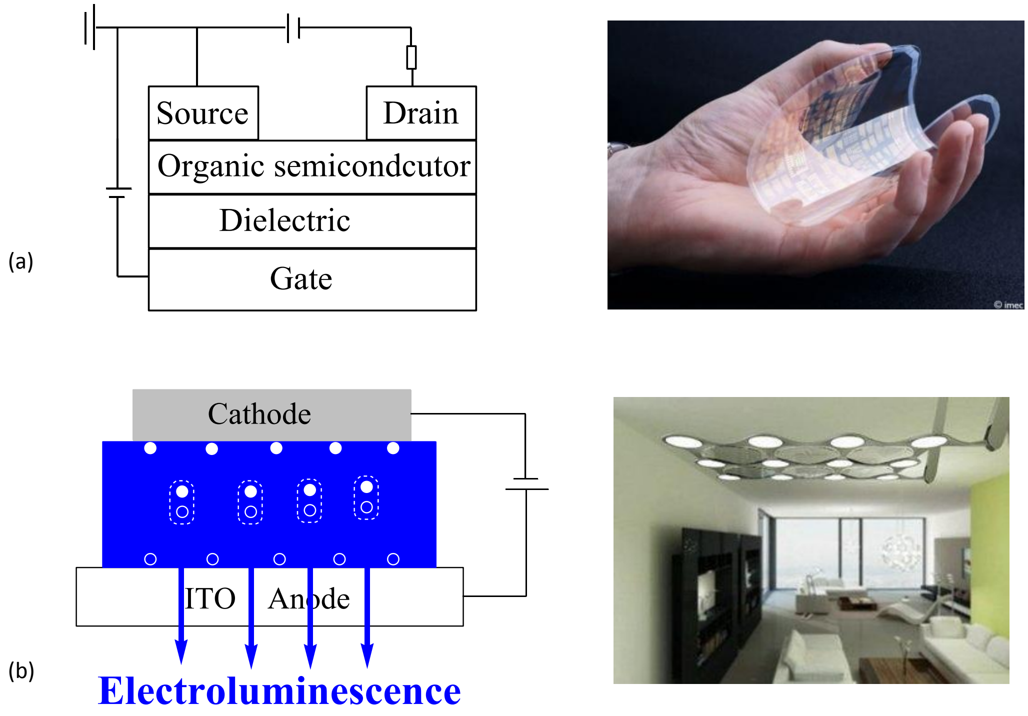


Figure 1. Organic semiconductors used in (a) OFETs (left) which has applications in flexible circuits (right) in RFIDs, e-paper and memory, (b) OLEDs which have applications in solid state lighting and displays.

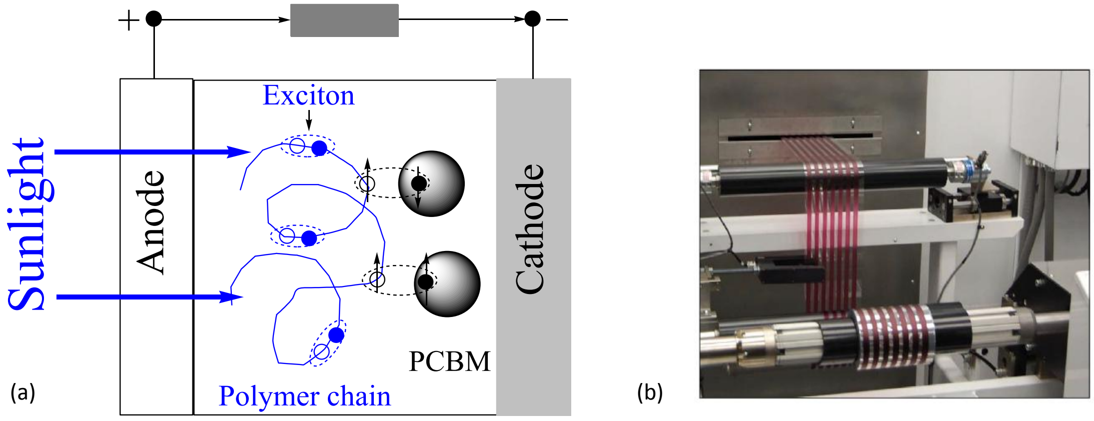
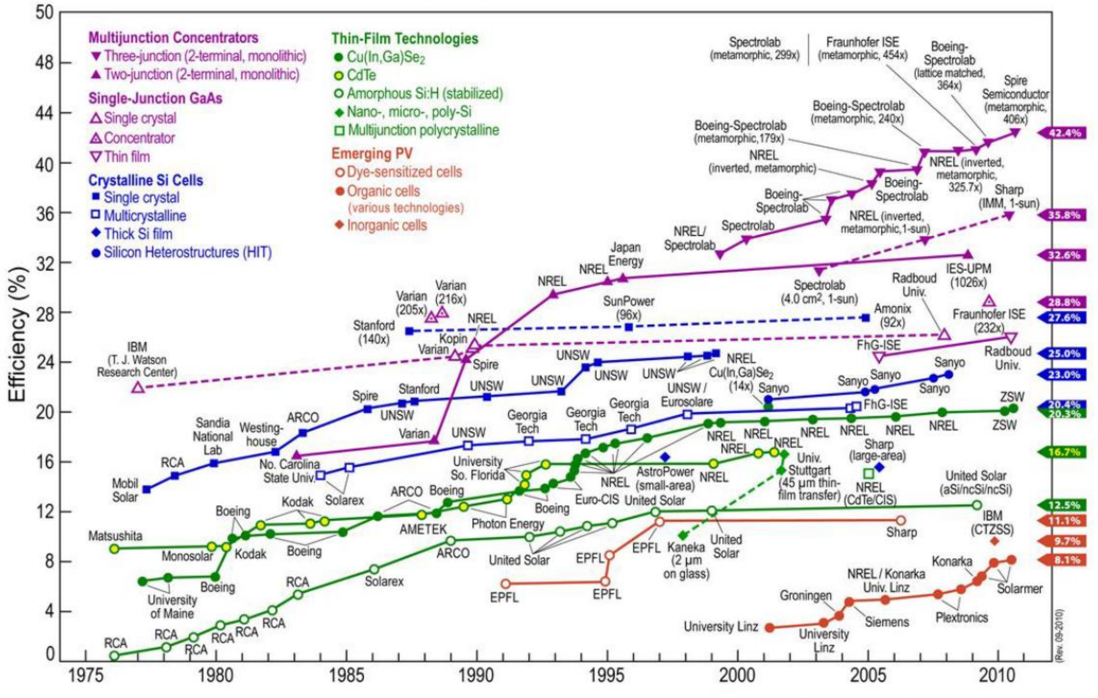


Figure 2. (a) Working principle of an organic solar cell. (b) Roll-to-roll processing can be used to create OPV which are lightweight and conformable.

2. Organic Photovoltaics & Comparision to Other Energy Harvesting Technologies

While crystalline silicon based PV cells and other inorganic materials such as CdTe and copper-indium/gallium-selenide/sulphide $Cu(In,Ga)Se_2$ (CIGS) account for 99% of the world production of solar cells, the need for high-temperature processing and high vacuum environments keeps the cost of these modules high. It is imperative that low cost alternative energy sources be found since fossil fuel reserves are limited and lead to CO_2 emissions, impacting global warming. In addition, worldwide demand for energy will be tripled by the end of the century, with current global energy usage at ~ 12 TW for 6.5 Billion people which is projected to reach ~ 20 TW for 8-10 billion people by 2050. The urgency for developing efficient renewable energies is even more pressing considering the demand arising from emerging economies, such as China, India and Brazil. In order to meet the DOE cost goal for achieving \$0.2/Watt, low cost, high efficiency PV technologies are actively being sought. Figure 3 surveys the various technologies that are currently in consideration for PV, from crystalline Si cells, multi-junction concentrators, thin-film technologies to emerging technologies which involves the use of nanomaterials,[10] and also includes organic PV technologies.

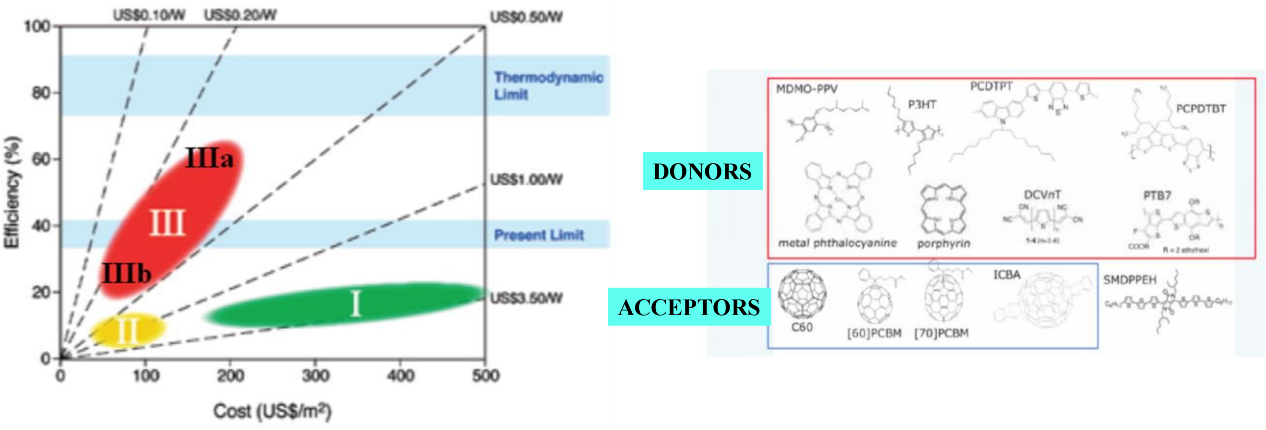


Source: *National Renewable Energy Laboratory, USA*

Figure 3. Comparison of OPV to other energy harvesting technologies. Source NREL.

Crystalline Si is considered a first generation (I) technology for PV, as exemplified in Fig 4a, where the power conversion efficiencies (PCEs) have reached ~ 25%. The second generation technologies (II) are based on thin films: amorphous Si, CdTe, and CIGS. While CIGS thin films have PCEs ~ 19 %, amorphous Si, although being cheaper than crystalline Si, has lower efficiencies ~ 12% and also suffers from stability issues which has limited its use in commercial applications. Third generation PV cells with ultrahigh efficiencies and/or ultra-low costs have been proposed, and if successful, would significantly reduce the cost-to-efficiency ratio and make solar electricity competitive against or even cheaper than fossil fuel generated electricity. Organic PV is a class of technologies that is considered to lie in this third generation PV cell technology (III).

The earliest report of photoconductivity in an organic compound was made in 1906 by Pochettino,[11] and subsequently the first organic solar cell was developed in 1986 by Tang and co-workers at Eastman Kodak.[3] A wide variety of new organic materials have now emerged,[12,13] as exemplified in Figure 4b; these include the development of conjugated p-type polymers such as regioregular poly(3-hexylthiophene) (P3HT) as the electron donors materials and fullerene derivatives, such as [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) or [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) as the n-type acceptors. Organic PV is also particularly attractive for integration with flexible materials such as clothes and tents. Considerable progress has been made in enhancing the PCE in OPV from less than 1% in the poly(phenylene vinylene) (PPV) system[7] to 4–5% in the poly(3-hexylthiphene) (P3HT) system in 2005,[14] to 10.6% achieved recently.[15] The significant progress seen in PCE in OPV can also be elucidated by the steeper slope of the OPV technology line in Fig. 3 in recent years, when compared to other energy harvesting technologies that have remained largely flat during the past 10 – 15 years, such as CIGS and amorphous Si. Despite the progress, challenges still lie ahead in improving PCE's in OPV further to make them economically competitive with other commercial technologies, as well as enhancing their operational stability.



(a)

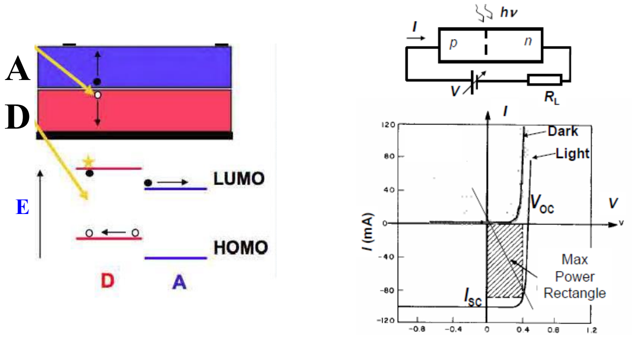
(b)

Figure 4. (a) Generation I, II and III solar cell technologies. OPV is considered to lie in Generation III due to its prospects for high efficiency and low cost. (b) Some representative materials used as p-type donors and n-type acceptors in organic solar cells.

3. OPV Device Operation and Architectures

Unlike the covalent bonding among atoms in inorganic semiconductors, the intermolecular interactions in organic semiconductors are characterized by van der Waals forces. This results in highly localized charges in organic semiconductors. Given the weak inter-molecular bonding in organic semiconductors, absorption of an incident photon leads to an exciton on one single molecule or on adjacent molecules, with a binding energy that ranges from 0.3 eV to 1 eV.[16,17] To generate electricity, excitons must be separated into free electrons and holes at the donor:acceptor (D:A) interface which is energetically tuned to split them into their opposite charges.

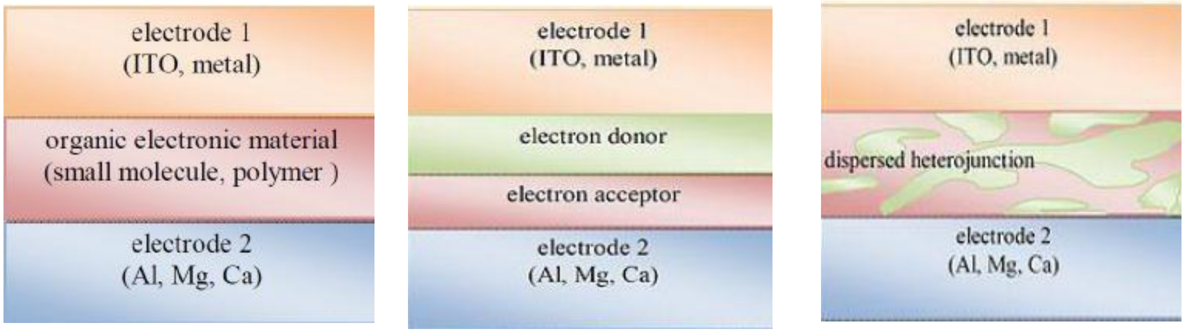
As shown in Figure 5, the exciton binding energy can be overcome with appropriate energy level alignment at the D:A interface. A rapid charge transfer process occurs leading to holes in the highest occupied molecular orbital (HOMO) of the donor material and electrons in the lowest unoccupied molecular orbital (LUMO) of the acceptor which results in charge dissociation.[18] After charges are separated, charge transport to the electrodes occurs via the built-in electric field, where holes are collected at the anode and electrons are collected at the cathode; this subsequently leads to a photocurrent in the external circuit as shown by the schematic in Fig. 5b. The diffusion lengths for such excitons in organic semiconductors is typically 5 – 15 nm before the respective electrons and holes recombine non-radiatively and give off their excess energy as heat.



(a) (b)

Figure 5. (a) LUMO and HOMO levels in the donor and acceptor materials of an OPV. (b) The IV characteristic showing the photo-current that is collected in the external circuit. The figure of merit for OPV (as with other PV technologies) is the V_{oc}, I_{sc} and the *FF*.

Historically, several device architectures have emerged for OPV, with the simplest device comprising of a single layer of the organic semiconductor sandwiched between electrodes as shown in Fig. 6a. However, such an architecture results in low power PCE since the electric field strength is not sufficiently large to break up the photo-generated excitons. A related architecture is the bilayer heterojunction, where the donor and acceptor layers are separated by a two dimensional D:A interface. However, due to this limited surface area, only excitons that are generated within 10-15 nm of this interface can diffuse to the interface, dissociate into free electrons and holes, and thus have the potential to contribute to the photocurrent. When excitons are generated far from this interface it is highly unlikely they can contribute to the photocurrent since they recombine non-radiatively and result in heat, prior to reaching the interface.



(a) (b) (c)

Figure 6. (a) Active layer is a single organic semiconductor layer that is sandwiched between the cathode and anode. (b) The heterojunction OPV architecture with a two-dimensional planar D:A interface. (c) The BHJ architecture which is a three-dimensional polymer blend where the D:A interface states lie.

The third architecture is the bulk hetero-junction (BHJ) device where a phase-separated blend of donor and acceptor materials are spatially distributed in a three-dimensional interpenetrating network which serves as the active layer. Depending on the blended ratio, nanoscale domains of 10-15 nm form and, as a result, almost every photo-generated exciton finds an interface within its diffusion length to dissociate into an electron and a hole.

Since the efficiency of BHJ devices exceeds that of bilayer devices, substantial effort has been placed in optimizing blended materials. The main challenge in the BHJ device architecture is to ensure effective charge transport and collection at the electrodes and to prevent any significant recombination from occurring.

Another architecture, the tandem solar cell architecture reported recently comprises of two solar cells in series in a vertical geometry where the two cells contain materials that have different absorption characteristics, in order to capture a wider range of the solar spectrum.

4. Factors Limiting Efficiency

Although the PCE of state-of-the art OPVs has already exceeded 8.6 %[19] and now reached 10.6%[15] more improvements are needed to enhance efficiency even further for practical applications. In particular, there is a need to simultaneously enhance the short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), and fill factor (FF)[20] as indicated by Eqn. (1), in order to enhance the efficiency η; here $I_{optical\text{-}power}$ is the incident optical power in Eqn. (2).

$$P_{\max} = V_{OC} I_{SC} FF \tag{1}$$

$$\eta_{\max} = \frac{P_{\max}}{I_{optical-power}} \tag{2}$$

The solar spectrum, depicted in Fig. 7, is very broad with most of the energy in the ultraviolet (UV), visible, and infrared (IR) spectral regions. Most of the solar energy is harvested by donor polymers but the organic materials used in the current state-of-the-art OPV cells, such as CuPc and P3HT, are effective at absorbing the UV and visible photons, and the IR photons are largely unabsorbed. Extensive research is currently underway to develop small band-gap conjugated polymers with band gap in the range of 1.2 - 1.9 eV to tap the IR portion of the solar spectrum which should help ensure higher J_{SC}.

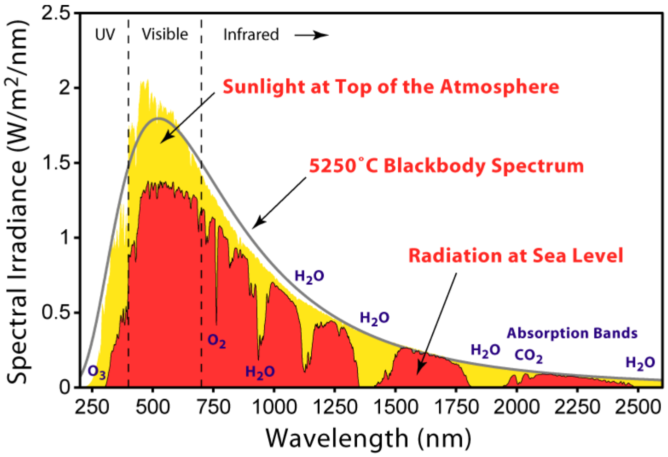


Figure 7. Radiation distribution of the solar spectrum.

Besides optimizing the band-gap of the donor polymer, the material should also have a low-lying HOMO energy level to offer high V_{oc} when blended with the acceptor layer. In addition, the energy offset between the LUMO energy levels of the polymer and the acceptor should be just large enough to provide a driving force for efficient charge separation, but small enough that it does not cause too much energy loss and hence reduce V_{oc}.

In BHJ solar cells, phase separation between the donor and acceptor materials impacts the ability for charge to be transported to the respective electrodes, which reduces J_{sc}. It is therefore critical to form an ordered morphology and interpenetrating donor-acceptor network for efficient extraction of photo-generated charges. It is also important to note that the low charge carrier motilities of the organic active layer will reduce the *FF* and thus high mobility materials are actively sought.

In addition, interfacial engineering[21,22] is an active area of research that is being pursued to minimize contact resistance between the active layer and the electrodes. This has led to efforts in interfacial engineering, including the use of self-assembled monolayers (SAMs), and metal oxides (TiOx and ZnO, etc.). Other approaches used recently to increase efficiency in OPVs involves the use of metal nanoparticles that exhibit localized surface plasmon resonances which enhance absorption and increases the photo-current.[23]

5. Summary

The organic PV area has shown tremendous progress in recent years with efficiencies that have reached 10-11% recently. Further improvements are necessary in order for OPV to compete with existing technologies. These improvements are likely possible through a combination of effective materials design including the development of low band-gap polymers, interface control, self-assembly of donor and acceptor phases, and device fabrication and engineering. Besides efficiency, work is necessary to enhance the lifetime and stability of the OPV solar cells to make them commercially attractive.

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REFERENCES

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[1] S. Reinke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem, and K. Leo, "White organic light-emitting diodes with fluorescent tube efficiency," *Nature* **459**, 234 (2009).

[2] D. Gundlach, "Low power, high impact," *Nature Materials* 6, 173 (2007).

[3] C. W. Tang, "2-layer organic photovoltaic cell," *Appl. Phys. Lett.* **48**, 183 (1986).

[4] L-M. Chen, Z. Hong, G. Li and Y. Yang, "Recent progress in polymer solar cells: manipulation of polymer:fullerene morphology and the formation of efficient inverted polymer solar cells," *Advanced Materials* **21**, 1434 (2009).

[5] Y. Liang, Z. Xu, J. Xia, S-T Tsai, Y. Wu, G. Li, C. Ray, and L. Yu, "For the bright future-bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%," *Advanced Energy Materials* **22**, E135 (2010).

[6] M. J. Currie, J. K. Mapel, T. D. Heidel, S. Goffri, M. A. Baldo, "High-efficiency organic solar concentrators for photovoltaics*,"* *Science* **321**, 226 (2008).

[7] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, "Polymer photovoltaic cells – enhanced efficiencies via a network of internal donor-acceptor heterojunctions," *Science* **270**, 1789 (1995).

[8] D. M. Chapin, C. S. Fuller, G. L. Pearson, "A new silicon p-n junction photocell for converting solar radiation into electrical power," *J. Appl. Phys.* **25**, 676 (1954).

[9] K. M. Coakley, M. D. McGehee,"Conjugated polymer photovoltaic cells," *Chem. Mater.* **16**, 4533 (2004).

[10] M. T. Borgstrom, J. Wallentin, M. Heurlin, S. Falt, P. Wickert, J. Leene , M. H. Magnusson, K. Deppert, and L. Samuelson, "Nanowires with promise for photovoltaics" *IEEE J. of Selected Topics in Quantum Electronics* **17**, 1050 (2011).

[11] A. Pochettino. *Acad. Lincei Rend.* **15**, 355 (1906).

[12] C. Bardeen, "Exciton quenching and migration in single conjugated polymers," *Science* **331**, 544 (2011).

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[13] M. Wang, X. Hu, P. Liu, W. Li, X. Gong, F. Huang, and Y. Cao, "Donor-acceptor conjugated polymer based on napthol[1,2-c:5, 6-c]bis[1,2,5]thiadiazole for high-performance polymer solar cells," *J. American Chemical Society* **133**, 9638 (2011)

[14] G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, "High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends," *Nature Mat.* **4**, 864 (2005).

[15] G. Li, R. Zhu and Y. Yang, "Polymer solar cells," *Nature Photonics* **6**, 153 (2012).

[16] I. G. Hill, A. Kahn, Z. G. Soos, and R. A. Pascal, "Charge-separation energy in films of π-conjugated organic molecules," *Chem. Phys. Lett.* **327**, 181 (2000).

[17] S. R. Forrest "The path to ubiquitous and low-cost organic electronic appliances on plastic," *Nature* **428,** 911 (2004).

[18] P. Peumans, A. Yakimov, and S. R. Forrest, "Small molecular weight organic thin-film photodetectors and solar cells," *J. Appl. Phys.*, vol. 93, pp. 3693 (2003).

[19] L. Dou et al., "Tandem polymer solar cells featuring a spectrally matched low-bandgap polymer," *Nature Photonics* **6**, 180 (2012).

[20] Z. He, C. Zhong, X. Huang, W.-Y Wong, H. Wu, L. Chen, S. Su, and Y. Cao "Simultaneous enhancement of open-circuit voltage, short-circuit current density, and fill factor in polymer solar cells," *Advanced Materials* **23**, 4636 (2011).

[21] Y. Zhu, X. Xu, L. Zhang, J. Chen and Y. Cao, "High efficiency inverted polymeric bulk-heterojunction solar cells with hydrophilic conjugated polymers as cathode interlayer on ITO," *Solar Energy Materials and Solar Cells* **1** (2011).

[22] J. H. Seo, A. Gutacker, Y. Sun, H. Wu, F. Huang, Y. Cao, U. Scherf, A. J. Heeger, and G. Bazan, "Improved high-efficiency organic solar cells via incorporation of a conjugated polyelectrolyte interlayer," *J. American Chemical Society* **133**, 8416 (2011).

[23] D. H. Wang, D. Y. Kim, K. W. Choi, J. H. Seo, S. H. Im, J. H. Park, O. O. Park, and A. Heeger, "Enhancement of donor-acceptor polymer bulk heterojunction solar cell power conversion efficiencies by addition of Au nanoparticles," *Angew. Chem. Int. Ed.* **50**, 5519 (2011).