

ORGANIC PHOTOVOLTAIC CELLS

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INTRODUCTION

Current conditions in the energy market are causing a shift in focus from limited, nonrenewable resources such as fossil fuels, to abundant, clean, and renewable resources such as wind, hydroelectric, and solar power. Solar power is currently harnessed in several ways, but the most familiar method involves the use of silicon-based solar cells. These inorganic solar cells have been highly optimized and can operate with efficiencies of greater than 12%. Widespread adoption of solar-based power has been hampered, however, by high manufacturing costs, difficulties tailoring the cells to various applications, and the inherent physical rigidity of silicon.

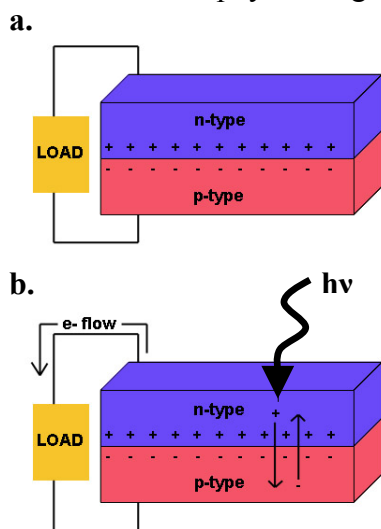


Figure 1. a) Normal p-n junction silicon solar cell under equilibrium conditions. b) Same cell producing free electron-hole pairs under illumination.

Organic photovoltaic (OPV) cells can overcome these problems because of the inherent ease with which many variants of an organic molecule can be synthesized. This synthetic flexibility allows the properties of the solar cells to be tuned to particular applications. The ability to add solubilizing groups to organic molecules also allows for the use of new and less costly techniques, such as inkjet printing, in the manufacturing process. Finally, organic molecules tend to have much more inherent physical flexibility, which could expand the range of applications to which solar cells could be used. The combination of lower costs and better adaptability should provide a boost in the desirability of solar power. Presented here is an overview of device operation and construction, molecule design, current progress towards the construction of viable OPVs, and the remaining hurdles to commercialization.

GENERAL OPERATION AND CONSTRUCTION

In silicon-based solar cells, phosphorus-doped silicon (electron-rich, n-type) and boron-doped silicon (hole-rich, p-type) are sandwiched together. At the interface between the two layers, an electrical field results from the initial migration of electrons from the n-type silicon to the p-type silicon, and the migration of holes (positive charges) in the reverse direction (Figure 1a). This process quickly reaches an equilibrium and forms a barrier to further charge transport. When light hits the cell, free electron-hole pairs are created, and these then migrate to the p-n interface where they separate due to the inherent

electrical potential-energy difference in the cell (Figure 1b). If no potential-energy gradient was present, then there could be no separation of the electron-hole pair. In addition, this potential energy difference also defines the upper limit of the photovoltage that is possible.¹

OPVs generally consist of a donor and acceptor, which are similar in concept to the two types of doped silicon. Unlike silicon solar cells, the donor and acceptor in an OPV are completely different materials. Each material has a characteristic HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy, with the HOMO and LUMO of the donor being higher in energy than their respective counterparts in the acceptor. The gap between the HOMOs and LUMOs is referred to as the optical band-gap (Figure 2a). This optical band-gap determines the minimum wavelength of light required for excitation in each material.

Photons hitting either donor or acceptor molecules excite an electron from the HOMO to the LUMO, but this does not generate a free electron-hole pair; rather, it creates a tightly coupled electron-hole pair called an exciton. This is due to the optical band-gap being smaller than the energy required to generate a free electron-hole pair.² In order to generate the free electron-hole pair, the exciton must travel to the interface between the donor and acceptor molecules or between the organic molecules and the electrode. At these junctions, electrons, which have been excited to the LUMO of the molecule, can jump into the LUMO of the acceptor, or holes in the HOMO can jump into the HOMO of the donor (Figure 2b). This dissociation can occur only if the difference in energy between the HOMOs or LUMOs is greater than the binding energy of the exciton. These phase-separated free electrons and holes then migrate to their respective electrodes. Efficient operation of an OPV requires that the exciton be able to reach an interface before recombination occurs.

OPV cells can be constructed in a variety of ways, including single layer, bilayer heterojunction, and bulk heterojunction cells.³ Single layer cells are the oldest and simplest examples. They consist of a metal-organic-metal sandwich. These early cells involved crystals of highly conjugated, polycyclic

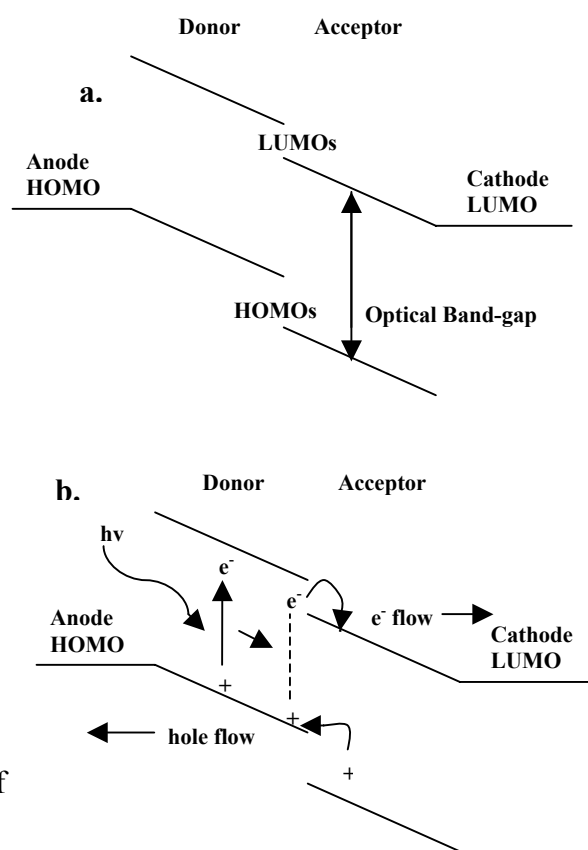


Figure 2. a) Generic OPV consisting of a donor and acceptor sandwiched between two electrodes. b) Same cell under illumination showing exciton formation, migration, and dissociation.

molecules. In 1959, Kallman and Pope reported on a cell that used a 5 μm anthracene crystal sandwiched between two NaCl solutions.⁴ The salt solutions functioned as transparent electrodes, which were further connected with silver electrodes. With these cells, the investigators were able to achieve an efficiency of only 2×10^{-6} %. Later, similar experiments were attempted using tetracene with distilled water serving as the transparent electrode.⁵ Eventually, in the late 70s, efficiencies as high as 0.7% were achieved with merocyanine-based cells.^{6,7}

These single layer cells have been mostly abandoned in favor of heterojunction cells, because in the latter the free electrons and holes are carried in completely separate phases, greatly reducing exciton recombination. The separate phases also allow the transport properties to be individually optimized for holes or free electrons. Bilayer heterojunction cells consist of a well-defined sandwich of anode, donor, acceptor, and cathode. The electrodes are chosen based on their matches with the HOMO of the donor and the LUMO of the acceptor. Bulk heterojunction cells are similar in that they also use separate donor and acceptor molecules. In the bulk heterojunction, however, the donors and acceptors are intimately mixed, rather than being placed in well-defined layers. The purpose of this OPV cell configuration is to reduce the distance an exciton must travel before reaching a donor-acceptor interface, which helps reduce the chance of exciton recombination.

MOLECULE DESIGN

The design and choice of efficient donor and acceptor molecules is of great importance. Candidate molecules must have optical band-gaps that are small enough to be excited efficiently by solar radiation. The majority of this radiation is produced in the visible and IR regions at wavelengths longer than ~ 450 nm, corresponding to a band gap of less than 2.75 eV. Donor molecules must be able to stabilize hole transport, and acceptor molecules must allow electron transport. The combination of donor and acceptor must be chosen to allow for the proper offset between their HOMOs and LUMOs. Finally, the molecules must be functionalized in a manner so that they can be solubilized for processing.

Donor Molecules

Donor molecules must satisfy several requirements in order to function efficiently. Absorption of visible or IR light is vital for the conversion of photons into excitons. After exciton formation, the donor molecule must allow for the movement of the exciton to a donor-acceptor interface and also possess a sufficient difference in HOMO to HOMO and LUMO to LUMO energy levels to allow for exciton dissociation. Once dissociation occurs, the hole must be stabilized as it moves back to the anode.

The absorption spectra of organic molecules in the UV-visible range are dominated by the $\pi \rightarrow \pi^*$ transitions of electrons. These transitions occur in unsaturated compounds and generally have very large molar absorptivities when compared to other transitions, such as $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$, or $\sigma \rightarrow \sigma^*$. The $\pi \rightarrow \pi^*$ transitions can be shifted from the UV to the visible by the inclusion of conjugated π -bonds. Each new π -bond adds a new π and corresponding π^* molecular orbital. As more π -bonds are added, the gap between the highest, filled π -orbital (HOMO) and the lowest, unfilled π^* -orbital (LUMO) shrinks. This smaller gap corresponds to a smaller energy (longer wavelengths) required for excitation. For this reason, polymers and organic small molecules used for photovoltaics are highly conjugated to promote visible light absorption. The conjugated system also allows for the movement of both electrons and holes along the molecule by delocalization of those charges. Holes can be preferentially stabilized through the use of electron donating groups.

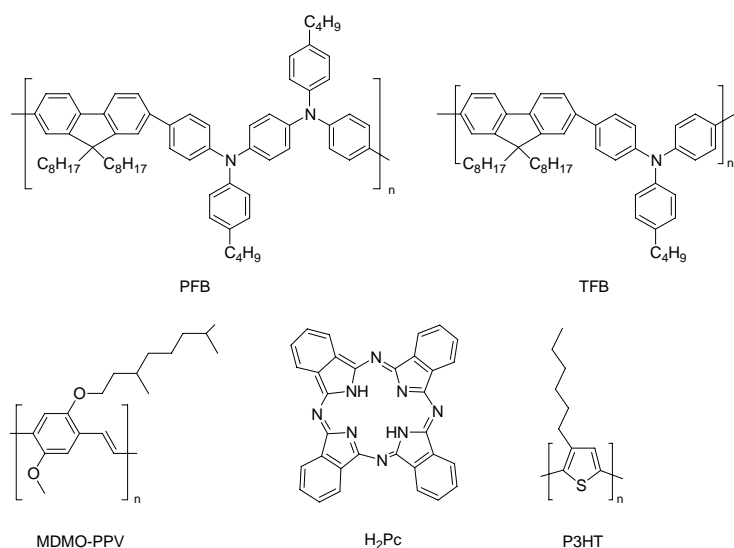


Figure 3. Examples of commonly used donor (p-type) polymers and small molecules: PFB (poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine)), TFB (poly(9,9'-dioctylfluorene-co-N-(4-butylphenyl)diphenylamine)), MDMO-PPV (poly((2-methoxy-5-(2,7-dimethyloctyloxy))-1,4-phenylenevinylene)), H₂Pc (phthalocyanine), and P3HT (poly(3-hexylthiophene-2,5-diyl)).

Acceptor molecules

Acceptor molecules must meet many of the same requirements as donor molecules with regard to absorption profiles, proper HOMO and LUMO interactions, and solubility. The major difference is the requirement that the acceptor molecule stabilize free electrons. This can be accomplished in one of two ways. Conjugated polymer chains can have electron-withdrawing groups added, such as CN or

Common donor molecules are shown in Figure 3. Each molecule is highly conjugated and possesses electron-donating atoms such as oxygen, sulfur or nitrogen. In many cases, the donating heteroatom is also used as the site of attachment for long alkyl chains, which improve solubility. The exception to this is phthalocyanine, H₂Pc, a porphyrin analog. Smaller organic molecules are generally much more soluble in organic solvents than polymers, so solubilizing chains are not necessary. If a particular phthalocyanine molecule is insoluble, attachments of long alkyl chains at the corners of the molecule can be used to improve solubility.

thiadiazoles, or C_{60} molecules, which have a high electron affinity, can be used with or without functionalization. Another important point to consider is the overlap of the absorption profiles for the donor and acceptor molecules. High efficiencies require that the maximum amount of solar radiation be absorbed. Using a donor-acceptor pair that overlaps as little as possible in the visible and IR regions ensures efficient absorption of the entire solar spectrum.

Figure 4 shows representative examples of acceptor molecules. The first two, CN-MEH-PPV and F8BT, are polymers and incorporate the aforementioned withdrawing groups. The third molecule, R-Ptcdi, can be derived from a tetracarboxylic acid bisanhydride by reaction with various

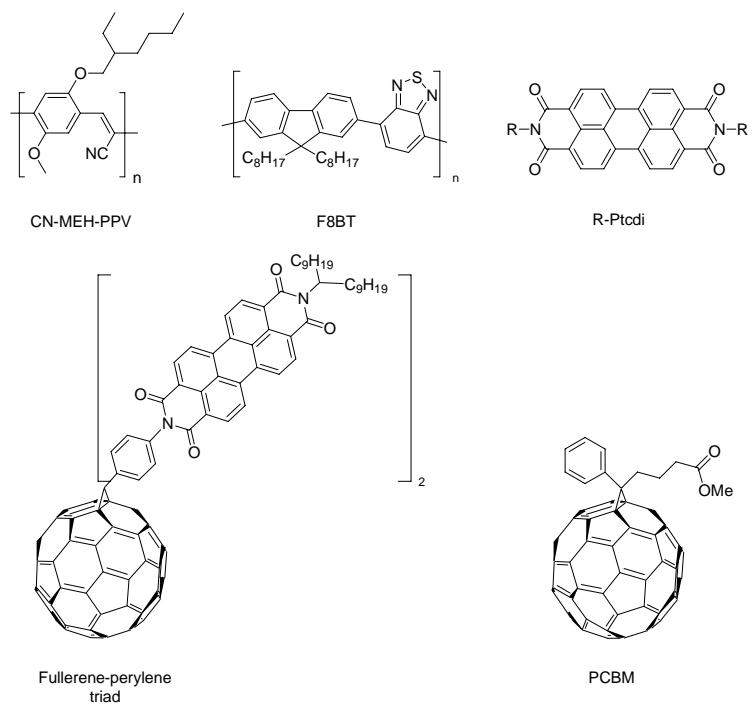


Figure 4. Examples of commonly used acceptor polymers and small molecules: CN-MEH-PPV (poly-(2-methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)-phenylene)), F8BT (poly(9,9'-dioctylfluorene-co-benzothiadiazole)), R-Ptcdi (N,N'-dialkyl-perylene-3,4,9,10-dicarboximide), PCBM (1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C₆₁), and a C₆₀ fullerene functionalized using a perylene derivative.

primary amines. Reaction with diamines such as benzene-1,2-diamine or naphthalene-2,3-diamine leads to imidazole products, such as benzimidazole and naphthoimidazole, respectively.⁸ The second row contains two modified C_{60} molecules. C_{60} has poor solubility, and the PCBM molecule was designed in an attempt to improve this characteristic. The other C_{60} derivative was prepared to improve the absorption characteristics of the molecule; while plain C_{60} and simple derivatives absorb at wavelengths shorter than 400 nm, the triad has extra absorption bands in the 450-550 nm region.⁹

REPRESENTATIVE EXAMPLES

As early as 1986, C. W. Tang had produced a bilayer heterojunction OPV using CuPc and the benzimidazole derivative of the perylene molecule that operated with an efficiency of ~1%. CuPc is formed from phthalocyanine in Figure 3 by complexation with a Cu^{2+} ion. This cell represented a significant improvement over the first OPVs and a slight improvement over the best monomolecular OPVs of Feng et al.^{6,7}

In 1995, Yu and Heeger produced a new type of cell called a bulk heterojunction, which had an efficiency of 0.9%.¹⁰ This cell was made from a mixture of the donor molecule, MEH-PPV, and acceptor molecule, CN-MEH-PPV, in a single organic layer between two metallic electrodes. While the efficiency of this OPV is not any better than that of Tang in 1986, these experiments demonstrated the viability of the bulk heterojunction design.

Starting early this century, vast improvements in OPV efficiency were achieved. Sariciftci et al. produced an OPV using a MDMO-PPV/PCBM blend that resulted in a 2.5% efficiency.¹¹ In addition, they also investigated how different solvents affected the nanomorphology of the blend and how those variations influenced efficiency. The blend was spin cast from both chlorobenzene and toluene, and the resulting cells were compared. Films spin-cast from toluene exhibited horizontal features of 0.5 μm and height variations of 10 nm, whereas much smaller features were found in films cast from chlorobenzene: horizontal features of 0.1 μm and height variations of 1 nm. The investigators attributed this increased uniformity to the greater solubility of PCBM in chlorobenzene. Notably, the more uniform films formed using chlorobenzene showed a ~280% increase in efficiency over those formed using toluene, 2.5% vs. 0.9%, respectively. The experiments of Sariciftci et al. plainly showed the influence of nanomorphology on efficiency. More recently, Forrest et al. have managed to achieve an efficiency of 4.2% using CuPc and pure C₆₀ in a bilayer heterojunction device.¹² Efficiencies this high have the potential to make OPVs viable, as long as the processing costs are not too high.

DEVELOPING AREAS

New ideas are emerging in both the synthesis of donor and acceptor molecules and in overall cell construction. A possible replacement for polymers is discrete oligomers. Polymer properties are not always well defined, and this can have a serious impact on OPV performance. The synthesis of specific oligomers would not only increase the uniformity of the device but also allow for greater tunability. Examples of discrete oligomer *p*-phenylenevinylenes are already known.¹³ Their stepwise synthesis allows for the selective introduction of a donor character at one end and an acceptor character at the other end, forming a donor-wire-acceptor compound (Figure 5). In an effort to insure that donor and acceptor moieties are close to each

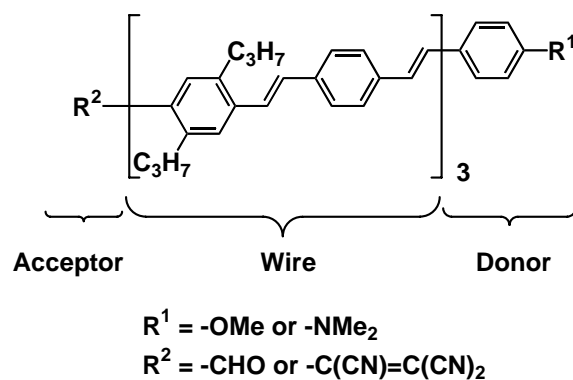


Figure 5 Examples of donor-wire-acceptor type molecules made using oligomers of polyphenylene vinylene

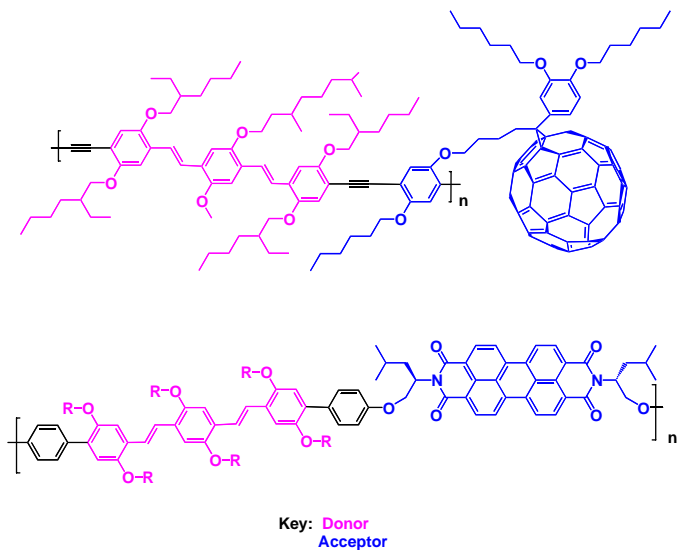


Figure 6 Examples of combined donor acceptor molecules. Top: PPV donor and pendant fullerene acceptor Bottom: PPV donor and perylene derivative acceptor

other to allow for efficient exciton dissociation, combined donor-acceptor molecules have also been synthesized (Figure 6).^{14,15} There is also an interest in the self-assembly of donor and acceptor molecules based on hydrogen bonding interactions.^{16,17,18}

CURRENT ISSUES

While the efficiencies of OPVs have been steadily increasing, there are still problems that need to be addressed. The processes that are normally occurring in the operation of OPVs are sequential oxidation and reduction reactions. Thus, overall, there should be no net change in the oxidation state of the organic molecules, as

the electrons make a full circuit. However, exposure to atmospheric oxygen and other contaminants can adversely affect the OPV's performance by permanently oxidizing or reducing cell components during fabrication or operation. In some cases, this process is extremely rapid, and cell activity is severely hindered after only a few hours. One solution is to perform cell fabrication under inert atmosphere conditions until the cell has been tightly sealed. This would complicate the manufacturing process and begin to negate the expected cost savings. A more satisfactory solution would be to modify the structure of the donors and acceptors. Improvement in the stabilization of the electrons or holes in general could prevent unwanted reactions from occurring while the molecular components are in the excited state. In this regard, it would be important to determine the site at which unwanted reactions are occurring and the mechanism by which they take place. Once these factors are known, better approaches could be taken to modify the structure so as to mitigate these reactions.

More complete absorption of the solar spectrum is also needed. The most strongly absorbing transitions are quite often less than 100 nm wide, so that even using two components with different optical band-gaps is not enough to give full coverage. The current solution to this problem is to stack multiple heterojunctions in a single cell.¹⁹ This has resulted in greater absorption in the visible region, with an overall cell efficiency of more than 5%. The increase in efficiency comes at the cost of complexity in the manufacturing of the cell. More research must be done in this area to determine whether greater improvements can be effected by molecular or structural modification.

CONCLUSION

The area of organic photovoltaics is rapidly advancing toward successful commercialization, and its progress mirrors that of organic light-emitting diodes (LEDs) a few years ago. The production of organic LEDs experienced many of the same issues that OPVs are now experiencing, such as limitations to long-term stability and the need to adapt to a wider range of wavelengths. These problems were overcome by a concentrated effort that was driven by the promise of cheaper and more versatile displays. OPVs offer a cheap and versatile way to power a multitude of devices. For this reason, it is likely that ways to circumvent the current obstacles in OPV fabrication and performance will be found, with the result that organic photovoltaic cells will become more economically viable and their use more commonplace. It is important to note that the sheer complexity of the cells' interactions at both the atomic and macroscopic levels requires the collaboration of chemists, material scientists, and engineers to fully maximize the potential of organic photovoltaics.

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