

Plastic photovoltaic devices

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The development of organic, polymer-based photovoltaic elements has introduced the possibility of obtaining cheap and easy-to-produce energy from light. Photoinduced electron transfer from donor-type semiconducting polymers onto acceptor-type polymers or molecules, such as C_{60} , is the basic phenomenon utilized in these photovoltaic devices. This process mimics the early photo-effects in natural photosynthesis. The polymeric semiconductors combine the photoelectrical properties of inorganic semiconductors with the large-scale, low-cost technology of polymeric 'plastic' materials. To date, devices with power conversion efficiencies of ~5% have been reported. Several companies and research institutions are focusing on this field now, making power conversion efficiencies up to 8-10% highly likely in the near future.

In a previous report in *Materials Today*¹, we introduced and discussed the basic principles and ideas of a plastic photovoltaic element developed in our lab. Using the photoinduced electron transfer at an interface between a semiconducting polymer donor layer, poly(2-methoxy,5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene) or MEH-PPV, and an acceptor C_{60} film, diodes were demonstrated with rectification ratios on the order of 10^4 . Significant improvement of the relatively low collection efficiency of the donor/acceptor bilayer was achieved by using phase-separated composite materials and controlling the morphology of the phase separation to give an interpenetrating network ('bulk heterojunction'). The power conversion efficiency of solar cells made from MEH-PPV/ C_{60} composites was increased by two orders of magnitude.

In the last 4-5 years, there has been an enormous increase in the understanding of the operational principle of polymer-based photovoltaic devices. This has led to a rapid increase in the power conversion efficiencies of such devices. To date, several labs have reported devices with power conversion efficiencies of ~4-5%. Given the stability of such products over a lifetime of around 10^4 hours, it is expected that such devices will enter niche markets soon.

The schematic structure of a typical polymeric photovoltaic device, as well as the different semiconducting polymeric donors and acceptors used in many research labs worldwide, is displayed in Fig. 1. In these devices, the

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photoactive layer is sandwiched between two metal (transparent conducting oxide) electrodes. The photoactive layers typically have a thickness of ~ 100 nm. Such thin layers have, of course, limited absorption even at the peak of their absorption spectrum. Because of the very high optical absorption coefficients of such polymeric 'dyes' (exceeding, for example, 10^5 cm^{-1}), this thin layer of ~ 100 nm still absorbs enough photons to deliver high photocurrents of ~ 10 mA/cm^2 . Nevertheless, the optical density has to be increased in such devices to *improve photon harvesting*. We have analyzed two possibilities:

- To achieve a higher absorption density, the thickness of the photoactive layer has to be increased to optimize absorption within the device, taking into account interference effects, which have to be calculated for each material and device configuration;
- The optical absorption of the photoactive layer does not match the photon flux from solar irradiation (Fig. 2). As

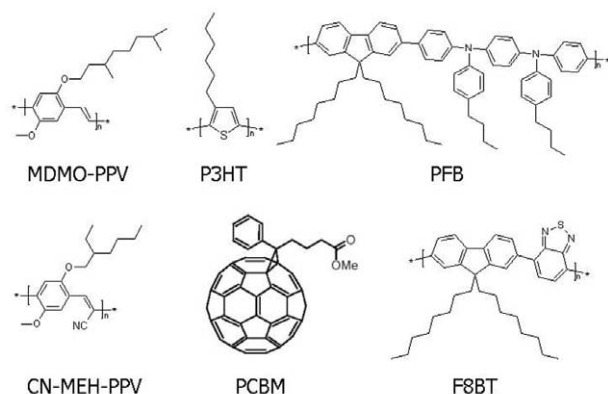
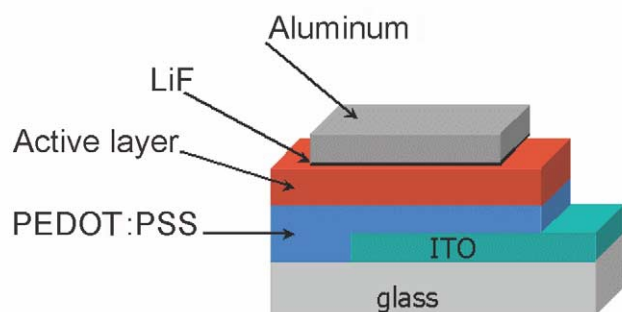


Fig. 1 Schematic structure of a bulk heterojunction photovoltaic device as well as the structural formulae of commonly used compounds in the active layer: poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV); poly(3-hexylthiophene) (P3HT); poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine) (PFB); poly(2-methoxy-5-ethylhexyloxy-1,4-phenylenecyanovinylene) (CN-MEH-PPV); [6,6]-phenyl- C_{60} butyric acid methyl ester (PCBM); and poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT).

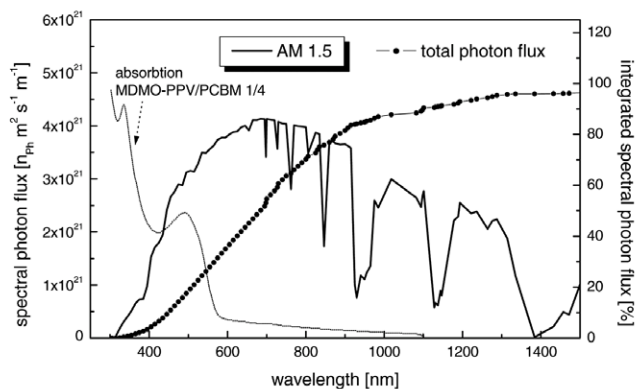


Fig. 2 Spectral photon flux of the AM 1.5 solar spectrum in comparison with the absorption profile of a MDMO-PPV:PCBM 1:4 film. Dotted line shows the total photon flux, i.e. percentage of photons available for a material with a certain band gap.

clearly demonstrated in Fig. 2, even assuming complete absorption of all photons above the band gap of the photoactive layer, we can only harvest at most 25% of the incoming solar light with an energy gap of around 2.1 eV. Fig. 2 further demonstrates that, by shifting the absorption edge to ~ 1 μm using smaller band gap semiconducting polymeric materials, we can predict an increase in photon harvesting by a factor of two to three, which could result in an increase of efficiency $>8\%$ by a conservative estimate.

Can the thickness of the photoactive layer simply be increased?

The trivial answer is yes. Indeed, technologically there is no obstacle to making much thicker films exceeding 1 μm . However, in polymeric semiconductors, the charge carrier mobilities can be as low as $\approx 10^{-4}$ $\text{cm}^2/\text{V}\cdot\text{s}$. This limits the possibilities for achieving fully operational devices with thick photoactive layers. Upon increasing the thickness of the photoactive layer, the series resistance becomes dominant and the short circuit current breaks down because of the low mobility of charge carriers. This effect can be modeled and, for the mobilities and absorption coefficients of polymers based on poly(*p*-phenylene vinylene) or PPV with fullerenes, one can estimate an optimum thickness of ~ 100 nm, which is indeed observed experimentally. Thus, simply making the photoactive material thicker to harvest more photons will not work. Instead, one needs to look for higher charge carrier mobility materials. Indeed, regioregular poly(3-alkylthiophenes) or P3AT have better mobilities and one can get higher photocurrents by increasing the thickness of

the layer. Since the mobility is also sensitive to the solid-state nanoscale morphology of a given system, different methods for improving the morphology should be applied too. For example, changing the solvent of the casting solution, as well as tempering of cast films, provide different optimization possibilities for determining the solid-state nanomorphology.

Can a shift to smaller band gap materials be realized?

Chemical synthetic tailoring of desired properties in polymeric semiconductor materials is at the cutting edge of current research. In Fig. 3, the different colors (energy band gaps) of different semiconducting polymers with slightly modified chemical structure are displayed. This flexibility is unique and cannot be achieved in classical inorganic semiconductors without artificial superstructures produced by hetero-epitaxy, for example. This flexibility in chemical tailoring is necessary, as discussed above, for matching the

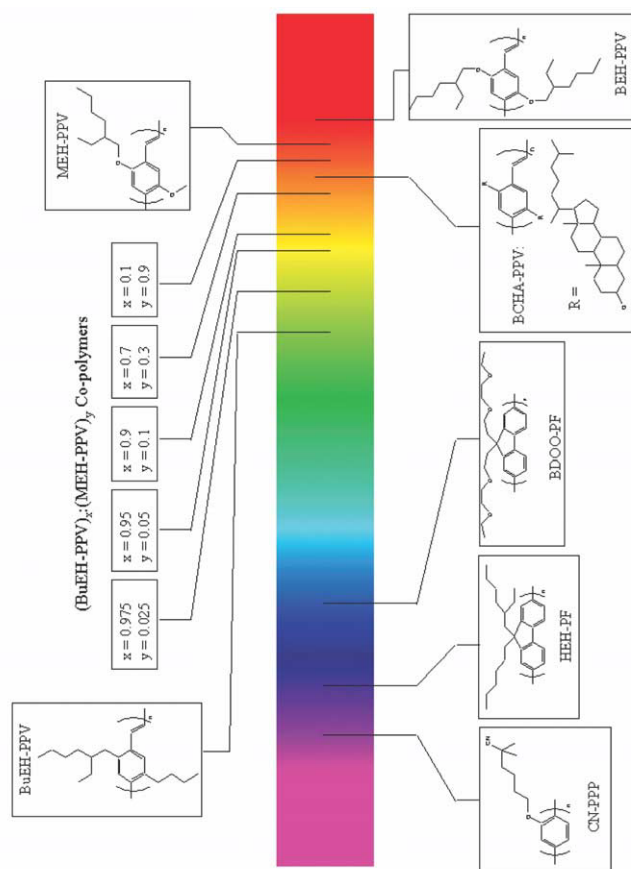


Fig. 3 Different colored semiconducting polymers can be achieved with slight modifications of the chemical structure, i.e. 'band gap engineering'.

absorption spectrum of the photoactive material to the solar emission spectrum. *Small band gap materials are therefore needed.* Several groups are attacking this problem and the results of these efforts are now emerging. Even though the optical absorption of some of these materials is shifted to the red and infrared regions of the spectrum, the ultimate success of a new polymer as a photovoltaic material is related to other properties as well.

What are the criteria for a successful material?

We analyze here the different steps for investigating a new material combination systematically:

- First, the photoinduced electron transfer from absorbing donor materials to electron acceptors in the photoactive blend has to be established. This criterion is necessary to generate photoinduced charges. The photoinduced electron transfer observed in mixtures of conjugated polymers with electron acceptors is a robust phenomenon, which is observed in nearly all nondegenerate ground state conjugated polymers. Therefore, for a new material based on polyheterocycles with similar ionization potentials around 4.5-5.5 eV, the photoinduced electron transfer has to be observed first. To achieve this, the photoluminescence quenching, photoinduced absorption, and light-induced electron spin resonance (LESR) should be monitored.
- The photoexcited charges have to be mobile. As such, the new materials have the additional task of transporting charges to the electrodes. The easiest and best check for this is to measure the incident photon to collected electron efficiency (IPCE), also known as external quantum efficiency (EQE), of a given solar cell configuration. It has been observed that, especially in acceptor materials, the *n*-type electron transport is heavily restricted or not possible at all. In such cases, even though the luminescence is quenched, photoinduced absorption shows the charged states, and all other photoinduced electron transfer criteria are fulfilled, there is no photovoltaic device efficiency. *Therefore, high charge carrier mobility materials are needed.*
- The electrodes of photovoltaic devices have to be selective in the case of bulk heterojunctions. Since bulk heterojunction devices comprise a mixed layer of donor-acceptor systems, there is *a priori* no symmetry breaking. Thus, by random diffusion processes, electrons and holes

will also travel to the wrong electrode and recombine there, contributing to loss mechanisms. Such diffusion and recombination effects can be reduced by thin devices with different work function electrodes that induce an electric field across the photoactive layer. This electric field has been shown to be effective in thin layer metal-insulator-metal (MIM)-type devices. In such a case, the charges are accelerated by the induced field and, thus, the selective transport and charge collection of the electrodes are established by the work function asymmetry. However, in thick devices, as well as under intense light soaking conditions such as AM1.5 solar simulated irradiation, the charges generated exceed 10^{18} cm^{-3} and, thus, start to screen the electric field induced by the electrodes. In this case, the diffusion will become important and dominate once again. Therefore, electron-blocking layers on the hole-collecting electrode and hole-blocking layers on the electron-collecting electrodes become important. In state-of-the-art devices, the role of the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) layer on an indium tin oxide (ITO) electrode and the LiF layer under an Al electrode can be rationalized in this manner (Fig. 1).

An example of an optimized device, using a regioregular poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) copolymer blended with [6,6]-phenyl- C_{61} butyric acid methyl ester (PCBM) with a very low series resistance and a high filling factor, is displayed in Fig. 4.

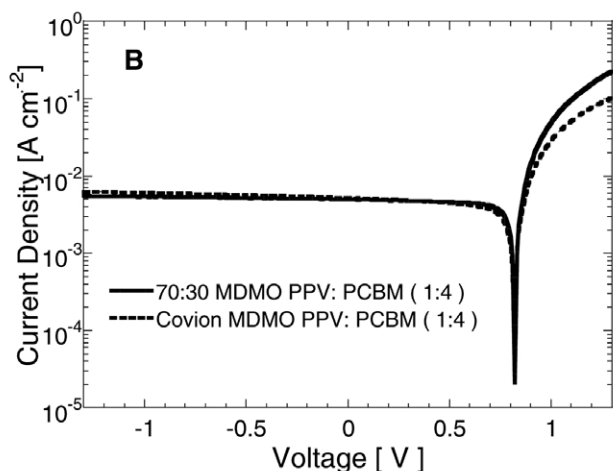


Fig. 4 Current density-voltage characteristics of bulk heterojunction photovoltaic devices based on 1:4 weight ratio mixtures of regioregular (70:30 copolymer) MDMO-PPV (solid line) and regiorandom MDMO-PPV (dotted line) in blend with PCBM. Fill factors up to 0.7 have been achieved.

Can the open circuit voltage be further increased?

In experiments on polymer/fullerene bulk heterojunctions, the open circuit voltage (V_{OC}) is found to depend strongly on the lowest unoccupied molecular orbital (LUMO) of the acceptor, as well as the highest occupied molecular orbital (HOMO) of the donor. Generally, the energy difference between the acceptor LUMO and donor HOMO levels defines the splitting of the *quasi*-Fermi-levels. In addition, the dependence of the V_{OC} on the fullerene content in the bulk heterojunction blend has been observed, which can be explained by the partial coverage of the cathode by the fullerene. Other experiments show that changing the electrode work function on either side also influences the V_{OC} , though to a smaller degree than expected from a MIM picture. Furthermore, the dependence of the charge transport levels on temperature and light intensity are reflected in the observed V_{OC} values. In conclusion, the V_{OC} is sensitive to a material's energy levels, as well as the engineering of interfaces and contacts. The V_{OC} at room temperature for the most efficient devices is ~ 0.8 - 0.9 V for MDMO-PPV blends with PCBM and 0.5 - 0.6 V for poly-(3-hexylthiophene) (P3HT) blends with PCBM. Further engineering of the V_{OC} can be achieved by increasing the gap between the HOMO level of the donor and the LUMO level of the acceptor.

Will organic, polymeric photovoltaic devices ever be stable enough?

The stability of such devices without any protection is extremely poor. It is imperative that polymeric photovoltaic elements are protected from ambient air. The comparison of large area photovoltaic cells fabricated in air without precautions such as dust- and/or oxygen-free production, and are either unprotected or protected with a special coating, clearly show that protection against air increases lifetime considerably. The plastic-based encapsulation technology of organic electronic devices will be a key technology for enabling many applications and is one of the major technical problems for realizing fully plastic light-emitting diode (LED) technology, as well as fully plastic chips. However, by employing glass-based encapsulation techniques, several companies have reported over 10^4 hours operational stability using accelerated test conditions.

On the other hand, plastic photovoltaic devices show advantages in product lifetimes and production yield. If a

small dark spot in an LED display occurs, the whole product becomes unusable, even though large parts of the display device are still operational. If a small part of a plastic chip is defective, the whole function of the chip is hampered, even though a large number of the integrated circuits are still functional. In photovoltaic devices, where a large-area integrated response is important, a defective part of the device will only result in a decrease in function of the active area in the vicinity. If no fatal shorts are produced, the device will still be within the specification limits, even though a small fraction of the area is unused. This advantage of plastic photovoltaic devices will be important in production lines, where actual product prices will be determined by production costs and production yield.

For large-scale power generation, the lifetime of photovoltaic devices directly determines the cost/watt peak. In high-power applications, today's organic photovoltaic devices (and probably those of the near future) will not be able to compete with crystalline Si solar cells, which have guaranteed lifetimes of tens of years. On the other hand, for many integrated product applications, the lifetime of the components need not necessarily be much longer than the lifetime of the whole product. In such applications, the integration of photovoltaic devices will require a lifetime slightly longer than the average lifetime of the whole product. Thus, the lifetime requirements of a photovoltaic device will be determined by the product itself. Today, there are several applications in consumer electronics,

packaging, labeling, and integrated textile products where the lifetime of plastic electronic components is superseding the lifetime of the product and will, therefore, be acceptable for the market.

Conclusion

The prospects for organic, plastic photovoltaic devices are improving as they get closer to market applications every day. This steady development is based on the optimization of the device physics:

- Optimization of the choice of metallic electrodes to achieve good ohmic contacts on both sides for the collection of oppositely charged photocarriers;
- Optimization of the choice of the donor/acceptor pair (the energy levels of the HOMO/LUMO influence the V_{OC});
- Optimization of the band gap and absorption profiles of the semiconducting polymer for efficient harvesting of the solar spectrum; and
- Optimization of the network morphology of the phase-separated composite material to maximize the mobility of the charge carriers within the different components of the bulk heterojunction.

In these areas, there is a vivid interaction between the fields of materials' synthesis, processing, characterization, and device fabrication in a synergistic, interdisciplinary manner. The prospects are good and, at a conservative estimate, a power conversion efficiency of ~8-10 % could be possible in the near future. **MT**

REFERENCES

1. Brabec, C. J., and Sariciftci, N. S., *Materials Today* (2000) **3** (2), 5
2. Simon, J., and Andre, J.-J., *Molecular Semiconductors*, Springer-Verlag, Berlin, (1985); Brabec, C. J., et al., (eds.), *Organic Photovoltaics: Concepts and Realization*, Springer-Verlag, Berlin, (2003)
3. Sariciftci, N. S., et al., *Science* (1992) **258**, 1474
4. Sariciftci, N. S., et al., *Appl. Phys. Lett.* (1993) **62** (6), 585
5. Yu, G., et al., *Science* (1995) **270**, 1789
6. Halls, J. J. M., et al., *Nature* (1995) **376**, 498
7. Sariciftci, N. S., and Heeger, A. J., Photophysics, charge separation, and device applications of conjugated polymer/fullerene composites. In *Handbook of Organic Conductive Molecules and Polymers*, Nalwa, H. S. (ed.), John Wiley & Sons, (1996), 414
8. Sariciftci, N. S., *Prog. Quant. Electr.* (1995) **19**, 131
9. Sariciftci, N. S., and Heeger, A. J., Conjugated polymer-acceptor heterojunctions; diodes, photodiodes, and photovoltaic cells. US Patent 5,331,183 (1994)
10. Morita, S., et al., *Solid State Commun.* (1992) **82** (4), 249
11. Morita, S., et al., *Jpn. J. Appl. Phys.* (1993) **32** (Part 2, No. 8B), L1173
12. Morita, S., et al., *J. Appl. Phys.* (1993) **74** (4), 2860
13. Fujii, A., et al., *Jpn. J. Appl. Phys.* (1996) **35** (Part 2, No.11A), L1438
14. Parker, I. D., *J. Appl. Phys.* (1994) **75** (3), 1656
15. Antoniadis, H., et al., *Polymer Preprints* (1993) **34** (2), 490
16. Granstrom, M., et al., *Nature* (1998) **395**, 257
17. Brabec, C. J., et al., *Adv. Funct. Mater.* (2001) **11** (1), 15
18. Halls, J. J. M., and Friend, R. H., In *Clean Electricity from Photovoltaics*, Archer, M. D., and Hill, R. (eds.), Imperial College Press, London, (2001)
19. Nelson, J., *Curr. Opin. Solid State Mater. Sci.* (2002) **6**, 87
20. Nunzi, J.-M., *C. R. Physique* (2002) **3**, 523
21. Shaheen, S. E., et al., *Appl. Phys. Lett.* (2001) **78** (6), 841
22. Schilinsky, P., et al., *Appl. Phys. Lett.* (2002) **81** (20), 3885
23. Padinger, F., et al., *Adv. Funct. Mater.* (2003) **13** (1), 85
24. Shaheen, S. E., et al., *Appl. Phys. Lett.* (2001) **79** (18), 2996
25. Dyakonov, V., *Physica E* (2002) **14** (1-2), 53
26. Schilinsky, P., *J. Appl. Phys.* (2004) **95** (5), 2816
27. Hoppe, H., et al., *Sol. Energy Mater. Sol. Cells* (2003) **80** (1), 105