Molecular Solar Cells

Hummelen, J.C.

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4.9 MOLECULAR SOLAR CELLS
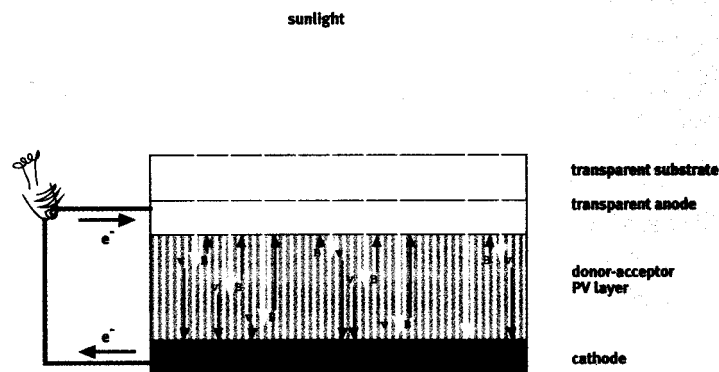
J.C. Hummelen[12]

Introduction

Sitting in a train and watching the world go by, you might occasionally see solar modules silently at work producing electricity. A steadily increasing number of buildings and boats are equipped with solar panels. You may find small photovoltaic (PV) arrays on emergency telephone boxes along interstate highways. These are only the very first messengers of what is planned to be a worldwide revolution in electric power production in the next 15 to 50 years.

At present, the active part of the typical commercial solar cells is made of silicon, either in the high-tech single-crystalline (sc-Si) form used in the chip industry, or in the cheaper and somewhat less-efficient multi-crystalline (mc-Si) form. The thickness of the silicon layer in these devices is on the order of 0.2 mm, making the material costs per square meter a real bottleneck in the competition with conventional (gas- and coal-based) electricity production. Nowadays, most research in photovoltaics is directed to thin-film devices (figure 4.9.1) [van Roosmalen, 1995]. In such solar cells, the thin photovoltaic active layer is supported by some low-cost supporting material, which can even be mechanically flexible. Micrometer-thin layers of amorphous silicon (a-Si), copper indium diselenide ($CuInSe_2$), or cadmium telluride (CdTe) as light absorbing materials are thick enough to absorb the bulk of the incoming light. Even thinner layers are sufficient when strongly absorbing organic dyes are used such as conjugated (containing alternating double and single bonds in the main chain) organic polymers and some low-molecular-weight organic dyes. They allow for a light-absorbing film thickness of only 100 to 300 nm, i.e. the molecular scale for polymers! A single monomolecular layer of a dye with 2-nm-thick molecules is not thick enough. However, nanocrystalline particles of semiconducting titanium

12 University of Groningen, Department of Organic and Molecular Inorganic Chemistry / Materials Science Centre
Nijenborgh 4
9747 AG Groningen
The Netherlands
J.C.Hummelen@chem.rug.nl

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dioxide (nc-TiO$_2$) can be sintered to obtain electrical (ohmic) contact between the particles. The resulting porous network of particles can subsequently be coated with a single layer of organic dye molecules. In that case, most of the incoming light is absorbed by the structure because the photons encounter many monomolecular layers. The latter is the principle of the solar cell developed by M. Grätzel, which is a product of nanostructured materials technology *avant la lettre*! [O'Regan, 1991] (section 1.2). In 1997, the best small-scale nanocrystalline TiO$_2$ dye cells turned the earthly solar spectrum of light into electric power with a conversion efficiency of ~10%, which is only a few percent less than the typical efficiency of commercial multicrystalline-Si-based photovoltaic modules. Other molecular photovoltaic devices based on organic molecules ('organic' or 'molecular' solar cells) show efficiencies below 2%, but new concepts are being developed that are expected to raise the efficiency significantly. Below, we will focus on these new concepts, especially on those involving nanostructured mixtures of (macro)molecular donor-acceptor pairs to yield 'plastic' solar cells.

Fundamental differences between inorganic and organic solar cells

In classic *inorganic* solar cells, a junction between two semiconducting materials (e.g. n-type Si and p-type Si) provides an internal electric field. Hence, when charges (electrons and holes; e$^-$ and h$^+$) are generated upon absorption of light, they move away from the junction in opposite directions. The charges can be collected at the bottom and the top of the device. The charge-carrier mobility in inorganic semiconductors is relatively high, hence, the charges can travel 'far' (hundreds of microns) without getting trapped.

In *organic* semiconductor materials, the charge-carrier mobility is invariably low. Inside the molecules the mobility can be very high. The fundamental problem is that the charges have to hop from one molecule to another many times in order to travel. Two molecules have to be really close and well-oriented in order

to allow for efficient charge hopping. Hence, crystalline organic materials (close and well-oriented molecules) and conjugated polymers (long molecules: less hopping if they are aligned in the right direction!) show the highest but still modest charge-carrier mobility. Liquid crystalline order can also help the hopping process.

Another fundamental difference between inorganic and organic semiconductor materials is present in the way the charges are generated: In organic materials, the initial step upon absorption of a photon is the formation of an electronically excited molecule in which the e^- and h^+ are only slightly separated and still tightly bound; i.e. an exciton. Depending on the type of material, this exciton can migrate somewhat like individual charges can, but one of the charges of the exciton has to be transferred to another molecule in order to form a truly separated pair of charges that can travel independently. The acceptor molecule has to be close to the donor molecule; otherwise the exciton doesn't survive the trip. Because of both mobility problems, organic solar cells, built with micron-scale-thick layered structures of donor and acceptor molecules like n-type and p-type layers in inorganic solar cells, don't function well. The scale of architecture in organic photovoltaic devices has to be brought down to the scale of the mobilities of the excitons and the separated charge carriers in these materials: the nanoscale.

Spontaneously nanostructured 'plastic' solar cells

A very elegant example of nanoscale architectural design for a molecular solar cell is known under the somewhat misleading term 'bulk-heterojunction' [Yu, 1995a; Halls, 1995]. In the ideal case, two regular, continuous, and interpenetrating networks of donor-molecules and acceptor-molecules make the photovoltaic active layer, sandwiched between two different electrodes. The donor and acceptor networks have two functions: first, upon irradiation, opposite charges are generated in each network; second, each network transports only one type of charges to the corresponding electrode. Because the bulk-heterojunction is not a junction in the semiconductor sense, i.e. it does *not* give rise to an internal electric field in the right direction for the charges to move to the electrodes, the electric field has to be provided by two electrodes with different work functions. This is no problem when a thin donor-acceptor film is used. The great nanotechnological challenge is how to obtain the ordered interpenetrating donor-acceptor networks structure in the film.

Although, until now, the principle of the bulk-heterojunction has been realized only in crude form, the photovoltaic efficiency results are very encouraging. Two kinds of bulk-heterojunctions are of special interest: one consisting of two types of conducting polymers (2CP cell) [Yu, 1995a; Halls, 1995] and the other consisting of a mixture of a conducting polymer and bucky balls (C_{60}) or, better, a fullerene derivative (CPC cell) [Yu, 1995b]. The 'two conducting polymers cell'
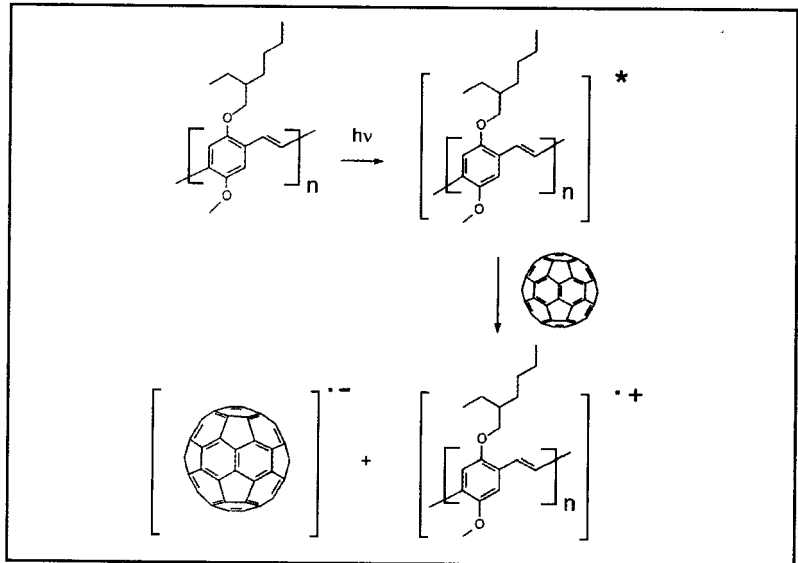
is made by simple spin-coating of a mixture of two conjugated polymers, one serving as the electron donor and transport medium for holes and the other as the acceptor and transport medium for electrons. Interpenetrating networks are formed spontaneously in the plane of the film. A nanostructured blend is formed because polymers do not mix well on the molecular level; they phase-separate when the solvent evaporates. The scale of the resulting morphology is in the nanorange quite often. Nanoscale morphology is also observed in a spin-cast film consisting of a mixture of a conjugated polymer and the molecularly perfectly spherical bucky ball [Yang, 1997]. Although such a phase segregation in blends of a conjugated polymer and other fullerenes has not been proven to exist, it is very likely that the functioning of solar cells made from this material is also based on the principle of a bulk-heterojunction.

Bucky balls serve as an electron acceptor in the combination with a number of conjugated polymers [Sariciftci, 1992]. The photo-induced electron transfer from the light-absorbing polymer to the fullerene occurs within an astonishingly short period of time: 0.3 picoseconds (3×10^{-13} s). This is so fast that no other disturbing process can compete. Hence, the efficiency of photo-induced electron transfer is 100% in this case. Moreover, since the electron transferred state can exist for as long as 1 ms, this allows for quite some time for the charges to be transported to the corresponding electrodes. That is a *very* good starting point for constructing a photovoltaic device! The basic events in this photoinduced electron transfer are depicted in figure 4.9.2.

Since a bucky ball is a low-molecular-weight spherical molecule, the percentage needed in the mixture with a conjugated polymer to obtain a continuous fullerene network is estimated to be ~ 15%. The limited solubility of bucky balls excludes the possibility to makes such mixtures. This problem has been over-

come by replacing bucky balls by soluble fullerene derivatives, resulting in the most efficient plastic solar cells known to date [Yu, 1995b].

Future directions for plastic solar cell research

The spontaneous nanostructure obtained in blends of conducting polymers (2CP) or of conjugated polymers and bucky balls (CPC) is still a very disordered one. Although the constituents most likely form continuous networks, they may be so irregular that the charge carriers have to travel small distances *against* the electric field supplied by the two electrodes. There is little doubt that this seriously hampers the efficiency of present plastic photovoltaic devices.

By designing building blocks that self-assemble and assemble with other mole- cules to make supramolecular architectural structures of high order, it should be possible to obtain more regular interpenetrating networks, preferably directed towards the electrodes. Making such nanostructures is a huge synthetic challenge! In figure 4.9.3, the present random interpenetrating network and a possible future form of a well-organized network are shown schematically. The fullerene component does not contribute significantly to the absorption of light by the photovoltaic device. Hence, the concentration of this component should be as low as possible in order to allow a thin film to absorb most of the incoming light. However, if the fullerene component has to serve as the electron transport network, it has to be present in an amount above the threshold for forming a continuous network (the percolation limit). This threshold would be lowered drastically if well-defined, soluble, and processable polymer forms of fullerenes would be applied.

At present, the conjugated polymers used in photovoltaic device research, have not been optimized for absorbing the solar spectrum of light. Important para- meters for conjugated polymers to be useful are: chemical purity, regularity, processability, band gap, ionization potential, stability, charge-carrier mobility, assembling sites, availability, and, eventually, cost of production. Optimizing the (nano)morphology of blends of conjugated polymers, a conjugated polymer

Figure 4.9.3
Left: a schematic view of the present random mixture of conjugated poly- mer and bucky balls (or fullerene derivatives).
Right: A possible form of a well- organized (supramolecular) mixture of a conjugated polymer and a fullerene derivative.
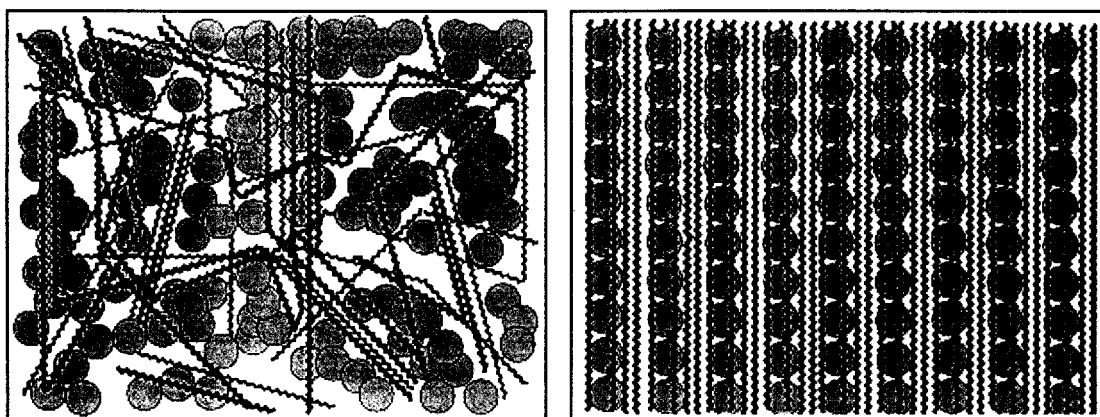
with a fullerene derivative, or mixtures of three components, is a new field with enormous potential for plastic photovoltaic devices.

Device stability, although expected to improve with increasing efficiency, is a major concern for molecular optoelectronic devices in general. Much can be learned from closely related areas of research such as photodiodes, molecular integrated circuits, nonlinear optical devices and light-emitting diodes. Light-emitting diodes based on self-assembling polymers have recently been realized on a lab-scale [Service, 1998].

Plastic solar cells can be envisioned to come in new formats, like in transparent (using infrared light only) or colored semi-transparent windows. Flexible and lightweight photovoltaic foil, that can be cut to the desired format, and that can be produced using relatively cheap methods like spaying or printing techniques, could find widespread application if it is stable for at least several years.