Alternating Copolymers and Alternative Device Geometries for Organic Photovoltaics

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Abstract The efficiency of conversion of light to electrical energy with the help of conjugated polymers and molecules is rapidly improving. The optical absorption properties of these materials can be designed, and implemented via molecular engineering. Full coverage of the solar spectrum is thus feasible. Narrow absorption spectra allow construction of tandem solar cells. The poor transport properties of these materials require thin devices, which limits optical absorption. Alternative device geometries for these flexible materials compensate for the optical absorption by light trapping, and allow tandem cells.

Keywords Photovoltaic energy conversion · Bulk heterojunctions · Polymer solar cell · Organic photovoltaics

INTRODUCTION

The conversion of sunlight-to-chemical energy occurs via photosynthesis using carbon-based molecules. A synthetic alternative to solar energy conversion utilize organic molecules and polymers to generate electrical energy. This form of energy conversion through organic photovoltaic systems shares some features of biological energy conversion systems, but deliver only electrical energy, and with an energy efficiency superior to biological systems (Blankenship et al. 2011). The choice of polymers and molecules allows design for optical absorption, electronic structure, and electrical transport. The disordered polymers give high-absorption coefficients but low electronic mobility. They are used in very thin film, but also allow flexible geometries. The low cost of materials and possibility of reel-to-reel production will dramatically cut costs for photovoltaic energy conversion; the energy payback

time is reduced by one to two orders of magnitude compared to crystalline silicon photovoltaics.

The steps of energy conversion in organic photovoltaic systems (OPV) (Dennler et al. 2009; Clarke and Durrant 2010; Deibel and Dyakonov 2010; Deibel et al. 2010) start with photon absorption in an organic compound, either a polymer of high molecular weight or a smaller molecule. The excited state created in this compound can be transferred throughout the system by exciton diffusion. This diffusion will bring the excited state close to an interface between two different molecules, of different electronic structure, electron donor, and acceptor. These two can be arranged in a planar geometry, in a bilayer of two different molecules (Tang 1986). They may also be blended in a bulk heterojunction, a mixture of two different polymer/polymer (Halls et al. 1995), molecule/molecule or polymer/molecule system (Yu et al. 1995). In all these three cases is the interface between a donor and an acceptor the critical point where charges are generated. These charges may then be left free to migrate or diffuse in an electrical field or concentration gradient, generating photocurrent, and photovoltage. As the sequel to charge generation, a charge transfer state is active to form separate charges; the role of this state in defining the photovoltage will be discussed below.

The performance of devices based on this physics has been progressing rapidly in recent years, with properly validated efficiencies between 8 and 9% reported (Green et al. 2011), and record efficiencies of 9.3% in simulated sunlight (Service 2011). While still inferior to the alternative technology for sunlight-to-electricity conversion based on organic molecules, the dye sensitized Grätzel cells, the gap is reducing rapidly. OPVs are purely electronic systems, where charges in the form of electrons and holes is the photocurrent; in the Grätzel cell ionic charge

Fig. 1 Normalized absorption spectra of some APFO, LBPP, and TQ polymers; the *inset* show the solar spectrum measured at the surface of the earth, with the sun at 45° above the horizon (the AM1.5G spectrum)

transport is essential, which requires low viscosity solvents. The comparison between the solid state OPV and the liquid-based Grätzel cells are therefore somewhat skewed, as the modes of application of these devices are quite different.

The main attraction of OPV lies in the small materials and energy input for energy conversion. Devices are planar multilayers of transparent electrode, active layer, and a reflective metal electrode, with additional functional layers at the electrodes. The thickness of the active absorber layer in OPVs is 100–400 nm; electrodes are 40–50 nm; functional layers are 1–10 nm. The total thickness of the device is less than 500 nm. The active material is a blend of organic compounds, with low costs of synthesis, all carbon based, and with no limitations on the global supply of constituent elements. When the transparent electrode is the doped metal oxide indium tin oxide, there are obvious supply problems, strong competition with the display industry and rapidly rising prizes, and this cannot be a economically viable solution for OPVs (Inganäs 2011). Alternatives abound in the form of doped polymer electrodes, in combinations with current collectors from metals. There is therefore a good match between the energy density in the solar radiation and the energy required to make the OPV; energy payback time is estimated to a few weeks in sunlight, in distinction to silicon photovoltaics where this is a number of years.

To maximize the energy conversion efficiency in OPV, overlap of absorption spectra of active materials with the solar spectrum and appropriate absorption strength to collect incoming light efficiently is required. Also, the photovoltage must be maximized. Electrical transport must be adequate to collect the photocurrent, and mobility of charge carriers must be balanced to avoid formation of space charges. Generation and recombination of charge carriers is the limiting step in many materials, and electronic transport is often sufficient from the transport point of view. Many of these aspects are compressed in the fill factor of the device, a current area of research.

DESIGNER POLYMERS

We have used new families of designer polymers based on alternating donor and acceptor moieties in the main chain conjugated polymer. An early polymer using the main chain polymer fluorene, with comonomers of donor–acceptor–donor segments of different chemical identity, gave promising results of high photovoltages (Svensson et al. 2003). Later developments within the family of this main chain polymer have greatly extended optical absorption properties to long wavelengths (1 μm) and matched electronic structure to the need for generating charge in blends with the fullerenes, C60 or C70 derivatives. These act as electron

Fig. 2 **a** Incoming solar light is dissipated between the active materials, electrodes (Al, PEDOT:PSS), and reflection as a function of wavelength, as calculated by matrix transfer theory and spectroscopic ellipsometric determination of the dielectric functions of the layer materials. The graph shows the distribution of optical power dissipation in the different layers, and reflectance, as a function of wavelength. **b** Alternative device geometry for trapping light and for making tandems. Folded cells with one or two materials. Incoming light is partially absorbed on first impact, but reflected light then is once more absorbed in the adjacent cell; these cells may be made from the same material, which leads to light trapping. If the materials are different, tandem combinations allows the division of the solar spectrum, between two materials. The standard geometry is a planar structure (not shown), with layers stacked on top of each other in tandem devices

acceptors and are essential for efficient photocurrent generation. Using phenylenes and fluorenes as main chain polymer has given us access to many polymers with suitable optical and electronic properties, including the appropriate electronic structure (Inganäs et al. 2009, 2010), but never delivering higher power conversion efficiencies than 4% in simulated solar light. More recently, using simple alternating copolymers of thiophenes with acceptors such as

quinoline, we have improved efficiencies to 6%, due to better spectral match with the solar spectrum, and more effective charge generation (Wang et al. 2010a) (see Fig. 1). Extending these structures with dimers of thiophenes moves absorption into the infrared, but does not improve efficiency at first (Wang et al. 2010b) but with improved processing comes to better than 6% (Wang et al. 2011).

The conflict between improving the optical coverage of the solar spectrum by moving to longer wavelengths/lower bandgaps, and the loss of photovoltage as the bandgap is thus reduced, is very prevalent in OPVs. Typically, moving beyond 700–800 nm is not rewarded with better conversion efficiency in the systems here reported. The determining factor for the photovoltage (Vandewal et al. 2009) is the charge transfer state created at the contact between donor and acceptor (Ruani et al. 2002), here the polymer and the fullerene, which can be observed in photocurrent generation and in electroluminescence upon charge injection (Tvingstedt et al. 2009; Zhou et al. 2009). The charge transfer state energy is directly related to the photovoltage, and predictions from a model based on Marcus electron transfer theory is corroborated by the temperature and the illumination intensity dependence of the photovoltage (Vandewal et al. 2010a). This is also in agreement with the Shockley–Queisser theory of upper limits to photovoltaic energy conversion (Vandewal et al. 2010b). Correlations between photovoltage and the HOMO of donor and LUMO of acceptor abounds in earlier literature (Gadisa et al. 2004), but the charge transfer state which is a hybrid between donor and acceptor wave functions is the primary determinant for photovoltage. It may not be the only state which can contribute to photocurrent, though (Tvingstedt et al. 2010).

Device geometries determine conditions for optical power dissipation in the sub-wavelength multilayer devices. Reflections at interfaces and interference between incoming and reflected waves determine both reflectance and absorption profiles. This can be easily modeled with the help of transfer matrix theory, and input to these models comes from spectroscopic ellipsometry of the different materials building the multilayer (Pettersson et al. 1999) (Fig. 2a). The loss of light due to reflection is considerable, and thicker layers reduce this loss. But thicker layers also means that the electrical field assisting the separation of charge carriers is lower, and that the length of transport of generated charges is increased, improving conditions for recombination and trapping, and leading to loss of photocurrent. Therefore, increased thickness is not generally a feasible strategy.

Improving light input into the active layers by nanostructuring for plasmon coupling (Tvingstedt et al. 2007b), microlenses for optical trapping (Tvingstedt et al. 2008) and milliscale structuring by folding cells into light traps

(Tvingstedt et al. 2007a) (Fig. 2b) have been attempted, and while all work, the only relevant contribution for low cost nonconcentrating photovoltaics comes from folding of flexible cells. Improvement of power conversion efficiency of incoming light by a factor of 1.7–1.8 can be obtained with this simple trick, which is just based on extending the optical path of solar light inside the active material (Fig. 2b). This is an opportunity that is easy with flexible thin film cells but quite difficult for high performance crystalline photovoltaics.

SUMMARY

In summary, OPV is a rapidly advancing technology with prospects for solar energy conversion of moderate efficiency and with superior economics in terms of input energy and materials, and with no limitations as to materials supply. It is therefore a possible technology in the desired rapid transition from an energy system based on fossil and nuclear sources to the plentiful supply of sunlight. Recent developments show that these technologies cannot wait for implementation. It is time for a major effort to bring efficiency up and production cost low, in order to enable this transition with flexible solar cells.

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