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Efficient polymer:polymer bulk heterojunction solar cells

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An organic bulk heterojunction photovoltaic device based on a blend of two conjugated polymers, a polyphenylenevinylene as the electron donor and a red emitting polyfluorene as the acceptor, is presented with a maximum external quantum efficiency of 52% at 530 nm and a power conversion efficiency, measured under AM1.5G, 100 mW/cm^2 conditions, of 1.5% on an active area of 0.36 cm^2. © 2006 American Institute of Physics. [DOI: 10.1063/1.2176863]

Solar cells based on conjugated polymers received a lot of attention since the discovery of the bulk heterojunction cell in 1995.[1] Polymer properties such as lightweight and mechanical flexibility may open niche markets for these solar cells. In addition, polymer solutions exhibit in general good film forming properties. This facilitates the use of high throughput production methods of these cells, which may lead to inexpensive solar cells with a reasonable efficiency and favourable mechanical properties.[2] Over the last decade, research efforts have led to ever increasing efficiencies, currently between 3% and 4% (AM1.5G, 100 mW/cm^2) for cells containing a conjugated polymer as electron donor and a fullerene as acceptor.[3–5] Other interesting approaches involve hybrid devices based on polymers and inorganic materials such as TiO_2,[6] ZnO,[7] $CdSe$,[8] and bulk heterojunctions prepared from a blend of two conjugated polymers.[9–11] The latter type of cells have not attracted as much interest as the polymer:fullerene or hybrid cells, which is quite remarkable since this concept may have certain advantages. In a polymer blend, both active materials can exhibit a high optical absorption coefficient and could cover complementary parts of the solar spectrum. Furthermore, it is relative easy to tune both components individually to optimise optical properties, charge transfer and charge collection processes.

Here we present a novel polymer:polymer bulk heterojunction solar cell based on a mixture of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) as the donor, and an alternating copolymer poly{9,9-dioctylfluorene-2,7-diyl-alt-1,4-bis[2-(5-thienyl)-1-cyanovinyl]-2-methoxy-5-(3,7-dimethyl-octyloxy)benzene} (PF1CVTP) as the acceptor.[12,13]

The syntheses of PF1CVTP (Ref. 13) and MDMO-PPV (Ref. 14) were described before as well as details on the optical measurements, cyclic voltammetry (CV) and transmission electron microscopy (TEM).[11] For devices, glass substrates were used with prepatterned, indium tin oxide electrodes (Philips Research). After cleaning and UV/O_3

treatment, a 60 nm layer of PEDOT:PSS (Baytron-P, H.C. Starck) was spin coated on the substrate. The photoactive layer was subsequently spin coated from chlorobenzene (Aldrich, HPLC-grade) solutions of the polymer mixture containing 0.3% eight of both components. The resulting layers had a thickness between 40 and 50 nm, as measured with a Dektak 8 surface profilometer (Veeco). Finally, a 1 nm layer of LiF (Aldrich) and 80 nm of Al (5N, Aldrich) were evaporated at 1×10^{-6} mbar through a shadow mask. In this way, four cells with areas of 0.10, 0.17, 0.36, and 1.0 cm^2 were obtained on the same substrate.

Electrical device characterization as well as sample annealing was carried out under N_2 atmosphere. For spectral response (SR) and incident light power (ILP) measurements a homebuilt setup was used with a tungsten/halogen lamp (12 V/50 W) and a Keithley SMU 2400 source measure unit. For the SR measurements the light was filtered using a set of 22 interference filters resulting in an illumination intensity of roughly 0.1–5 mW/cm^2 depending on the wavelength. For the ILP measurements a combination of five neutral density filters was used. A Spectrolab XT-10 solar simulator was used to measure the power conversion efficiency under standard test conditions (AM1.5G, 100 mW/cm^2). For these measurements, devices were placed in a sealed sample holder filled with nitrogen. The devices were illuminated through a glass window, causing additional absorption and reflection losses ($\sim$10%), for which was not corrected. The short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), maximum power point, and the power conversion efficiency (η_e) are determined using standard definitions and methods.[15] The particular combination of the test and calibration cell (a monocrystalline Si cell with a KG1 filter, calibrated at Fraunhofer ISE, Freiburg, Germany), together with the spectrum of the solar simulator and the tabulated AM1.5G spectrum resulted in a mismatch factor of 0.88.

A photovoltaic effect was observed in the 'as prepared' devices, however, the devices were significantly improved upon thermal treatment of 135 °C$\pm$2 °C for 10 min, as found in earlier experiments.[4,11] The best devices were pre-

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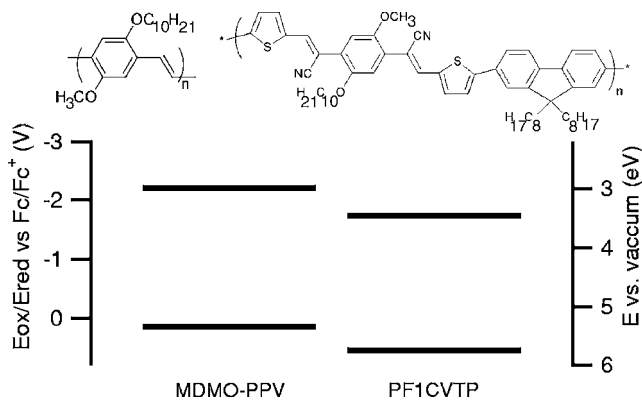[a]Electronic mail: marc.koetse@tno.nl
[b]Electronic mail: veenstra@ecn.nl

FIG. 1. Structures, redox potentials (left axis), and energy levels (right axis) of the donor (MDMO-PPV) and acceptor (PF1CVTP) materials.

FIG. 3. *J-V* curve measured under standard conditions (AM1.5, 100 mW/cm²). The open circles indicate the dark current curve, the solid squares the current under illumination. The inset shows the EQE of this particular cell (solid squares) and cell with the highest EQE. The latter cell was prepared without the additional top layer (+).

pared with an additional thin layer (~5 nm) of the acceptor material between the photoactive polymer blend (layer thickness 45 nm) and the electron collecting electrode. This layer is spin coated from a saturated acetone suspension (~1 mg/ml) onto the polymer blend film.

The chemical structures as well as the oxidation and reduction potentials of the materials measured by CV are shown in Fig. 1. The electron affinities and the ionisation potentials were deduced from these potentials, assuming an energy of 4.7 eV against vacuum for the Ag/Ag⁺ electrode and 0.5 eV for Fc/Fc⁺ against Ag/Ag⁺. The onset of the reduction wave of PF1CVTP is located at −1.75 V vs Fc/Fc⁺, and the oxidation onset was found at 0.55 V. Compared to MDMO-PPV ($V_{red}=-2.21$ V and $V_{ox}=0.15$ V vs Fc/Fc⁺), the electron affinities differ by 0.45 eV and the ionisation potentials by 0.40 eV. By applying a method described by Halls *et al.*[16], we find that the lowest charge transfer transition (E_{inter}) is about 0.2 eV below the lowest intramolecular transition (E_{intra}).[17] Thus, charge transfer seems energetically favoured over energy transfer.[16,18]

Optical measurements corroborate this assumption. Figure 2 shows the normalized UV-visible absorption and photoluminescence (PL) spectra for thin films of MDMO-PPV (squares) and PF1CVTP (circles) spin coated on quartz substrates with a layer thickness varying between 40 and 50 nm. MDMO-PPV has an absorption maximum of 517 nm with an

onset of 595 nm. The absorption maximum for PF1CVTP is 473 nm and the onset is at 575 nm. Films of the pure materials were found to be highly luminescent, while the luminescence of a film of the blend is significantly quenched by a factor of 10 as compared to the luminescence of the acceptor material. Annealing increases the quenching to a factor of 20. The incomplete luminescence quenching indicates that photophysical processes other than charge transfer are not quantitatively suppressed. Morteani *et al.*[18] and Offermans *et al.*[19] investigated the optical properties of conjugated polymer donor-acceptor blends in detail. They identified a complicated interplay between several competing decay channels. Nevertheless, the significant photoluminescence quenching combined with the fact that charge transfer is energetically favorable are two a strong indicators that this system may be useful for photovoltaic applications.

A representative *J-V* curve of a cell with an active area of 0.35 cm², measured under standard test conditions is given in Fig. 3, yielding a J_{sc} of 3.0 mA/cm², a V_{oc} of 1.40 V and a FF of 0.37, corresponding to a power conversion efficiency of 1.5%. Cells with different active areas gave similar results.

The inset in Fig. 3 presents the external quantum efficiency of the same cell (solid squares). The spectrum is recorded at low light intensities. The calculated AM1.5G, 100 mW/cm² short-circuit current density from this plot is 3.8 mA/cm². The difference between the actual and calculated current is due to two effects: a sublinear dependence of the J_{sc} on the incident light power (~ILP$^\alpha$, with $\alpha=0.93$), probably caused by recombination processes, and additional reflection and absorption losses due to the use of an extra glass window in case of the *J-V* measurements under the solar simulator. The other line (crosses) in the inset of Fig. 3 shows the spectrum of another sample with even higher external quantum efficiency. This sample was optimized for high EQE. The cell was prepared without the additional acceptor layer on top of the blend layer. The maximum EQE found for this device was 52% at 530 nm. However, the power conversion efficiency was slightly lower (1.4%) due to a lower ILP dependence ($\alpha=0.90$) and a lower fill factor (0.34).
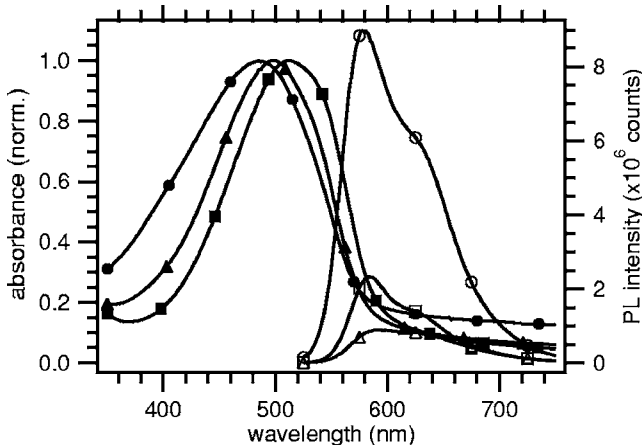

FIG. 2. Absorption (solid markers) and photoluminescence (open markers) spectra of MDMO-PPV (squares), PF1CVTP (circles), and blend without additional top layer and thermal treatment (triangles). Photoluminescence spectra are corrected for differences in layer thickness.
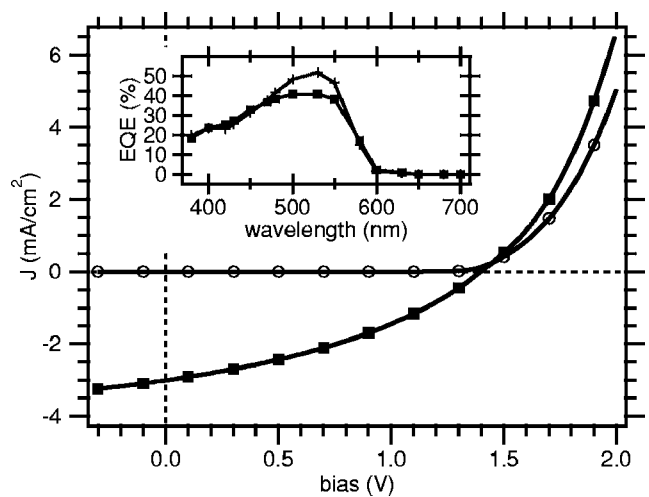
We note that these high external quantum efficiencies proof indirectly that the polymer blend adopted a suitable morphology. Attempts to reveal the organization of the two components within the photoactive layers were made by using conventional TEM. However, the TEM images of freshly prepared as well as of annealed layers only showed homogeneous films without recognizable features. Apparently, the nature of these films makes it hard to detect phase separation using conventional TEM as we have shown previously using energy filtered TEM.[20] Therefore, we are cautious to claim that no large-scale phase separation occurred in the photoactive layer. This will be part of future studies.

The quantum and power conversion efficiencies reported here, are among the highest reported efficiencies for polymer:polymer photovoltaic cells.[10] This shows the potential of polymer:polymer bulk heterojunction solar cells to become a useful player in the quest for inexpensive, large area, flexible photovoltaics.

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