# Photoinduced Electron Transfer and Photovoltaic Response of a MDMO-PPV:TiO$_2$ Bulk-Heterojunction**

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Scheme 1. Structure of MDMO-PPV.

Dye-sensitized TiO$_2$ solar cells have attracted considerable interest since it was shown that conversion efficiencies of up to 10 % can be reached.[1,2] In recent years successful attempts have been made to replace the liquid electrolyte solution in these cells with elastomeric polymers or gelators filled with an ionic redox couple,[3–7] and by p-type organic or inorganic semiconductors,[1–3,8] resulting in conversion efficiencies of up to 3.2 %.[4] A particularly attractive approach is to replace the dye and liquid electrolyte with a single conjugated polymer which combines the functions of light absorption and hole transport.[5–9] However, one of the problems associated with conjugated polymers and nanocrystalline TiO$_2$ (nc-TiO$_2$) is the inefficient filling of the pores of the TiO$_2$ matrix, especially because small (~20 nm) pores are required to ensure that the majority of photoexcited charge carriers in the polymer reach the interface with TiO$_2$ where charge separation occurs. In practice, hybrid polymer/nc-TiO$_2$ photovoltaic devices are now limited by charge transport (incomplete filling) and charge generation (large pores).

Here, we present a new and simple procedure for preparing bulk-heterojunction hybrid organic–inorganic solar cells in which a continuous interpenetrating network of TiO$_2$ is created inside a thin conjugated polymer film. The characteristic distance of the polymer:TiO$_2$ bulk-heterojunction is in the nanometer range and results in an efficient formation of photoinduced charges that can be collected when the film is incorporated in a photovoltaic device.

To prepare the bulk-heterojunction, a dry tetrahydrofuran (THF) solution containing poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylene vinylene] (MDMO-PPV; Scheme 1) and titanium(IV) isopropoxide (Ti(OC$_3$H$_7$)$_4$), a precursor for TiO$_2$, is spin-coated on a substrate to obtain a mixed film with a thickness of about 50–70 nm. Subsequent conversion in the
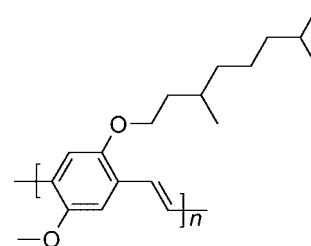
dark of the Ti(OC$_3$H$_7$)$_4$ precursor via hydrolysis in air results in the formation of a TiO$_2$ phase in the polymer film. As a consequence of the presence of TiO$_2$, the bulk-heterojunction film becomes resistant to scratching and can no longer be wiped off the substrate. Furthermore, the polymer in the bulk-heterojunction no longer dissolves in organic solvents such as toluene.

X-ray photoelectron spectroscopy (XPS) has been used to assess the formation of TiO$_2$ under these conditions by examining the C/Ti and Ti/O elemental ratios, which are expected to change from 12:1 and 1:4 in Ti(OC$_3$H$_7$)$_4$ to 0:1 and 1:2 in TiO$_2$. Because the elemental composition is strongly influenced by the polymer in the film, the conversion of Ti(OC$_3$H$_7$)$_4$ into TiO$_2$ under ambient conditions (in the absence of polymer) was also studied and compared to a film of TiO$_2$ prepared via the same procedure followed by conversion at high temperature (400 °C) in air for 30 min. Both samples were then placed under vacuum overnight. The XPS spectra of the low- and high-temperature converted pure Ti(OC$_3$H$_7$)$_4$ films were found to be very similar and to have binding energies for Ti^{4+}(2p$_{3/2}$), O(1s), and C(1s) of 459.0, 530.4,[10] and 285.0 eV (Fig. 1a), in agreement with literature data.[11,12] Assuming that no adsorption of carbon-containing material has occurred, the maximum conversion for the film treated at 400 °C is 95 %, based on the C/Ti ratio. Based on the ratio of the O(1s)(Ti–O–Ti) peak at 530.4 eV and the O(1s)(Ti–O–X, (X = C, H)) contribution at 531.9 eV, the minimum conversion for this film is 87 %.[10] For the Ti(OC$_3$H$_7$)$_4$ film converted at room temperature, the maximum and minimum conversions obtained in this way are 91 and 77 %, respectively. The XPS spectrum of a 1:1 (v/v) MDMO-PPV:TiO$_2$ bulk-heterojunction is very similar to that of nc-TiO$_2$ (Fig. 1a). After correcting for the small O(1s) contribution of MDMO-PPV (obtained from a pristine MDMO-PPV film), the conversion of Ti(OC$_3$H$_7$)$_4$ into TiO$_2$ in the bulk-heterojunction is estimated to be at least 65 %, somewhat less than for pure Ti(OC$_3$H$_7$)$_4$. The upper limit for the conversion cannot be calculated because the XPS C(1s) signal is dominated by the contribution of the polymer. Because no thermal annealing step is used in the preparation, amorphous rather than crystalline TiO$_2$ is formed.[13]

The UV-vis spectrum of the MDMO-PPV:TiO$_2$ bulk-heterojunction (not shown) clearly reveals the presence of MDMO-PPV from the strong π–π* transition in the visible region. Bulk-heterojunctions with 1 %, 2 %, 5 %, 10 %, 25 %, and 50 % volume of TiO$_2$ have been prepared and reveal that

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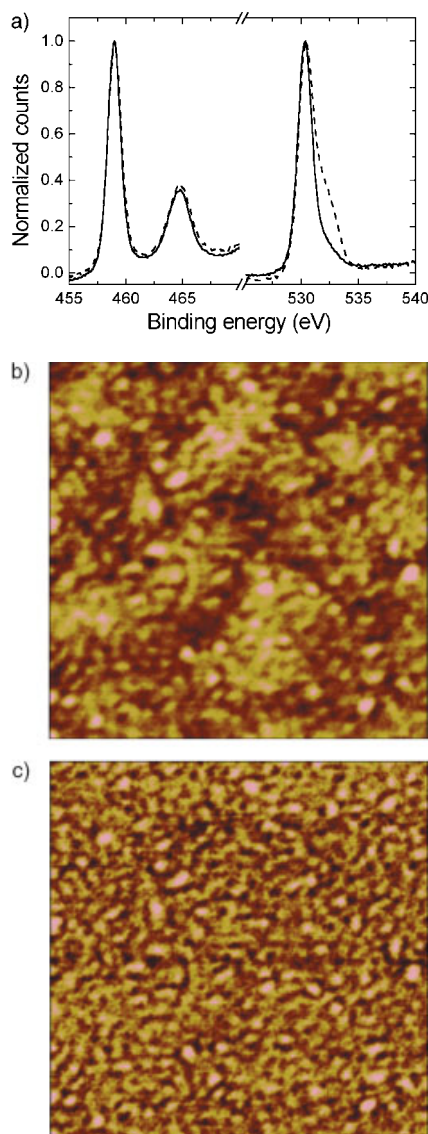P.O. Box 513, NL-5600 MB Eindhoven (The Netherlands)

Fig. 1. a) XPS spectra of nc-TiO$_2$ after annealing at 400 °C (solid line) and of the 1:1 (v/v) MDMO-PPV:TiO$_2$ bulk-heterojunction (dashed line). b) Tapping mode AFM height image of a 1:1 (v/v) MDMO-PPV:TiO$_2$ bulk-heterojunction (2 μm × 2 μm, z-range = 10 nm). c) Corresponding AFM phase image (z-range = 7.5°).

with an increasing amount of TiO$_2$, the absorption maximum of MDMO-PPV at $\lambda = 500$ nm shifts slightly to shorter wavelengths (15 nm at 50 % TiO$_2$). Possibly, TiO$_2$ prevents aggregation of MDMO-PPV chains in the solid state.

The morphologies of MDMO-PPV:TiO$_2$ bulk-heterojunctions with varying volume ratios were studied using tapping-mode atomic force microscopy (AFM). The topographic image of the 1:1 (v/v) MDMO-PPV:TiO$_2$ bulk-heterojunction reveals a smooth surface with a root-mean-square roughness of a few nanometers (Fig. 1b). The corresponding phase image is more resolved and shows lateral phase differences with a characteristic distance of roughly 50 nm (Fig. 1c). The light-colored micro-domains were found to decrease in size for films with less TiO$_2$ present.

The photoluminescence (PL) at 580 nm of the MDMO-PPV:TiO$_2$ bulk-heterojunction is significantly quenched compared to that of a pristine MDMO-PPV film. Monitoring the PL intensity as a function of the volume fraction of TiO$_2$ (Fig. 2a) reveals that the PL decreases with increasing amount of TiO$_2$, and is quenched by a factor of 19 in the 50 % blend.
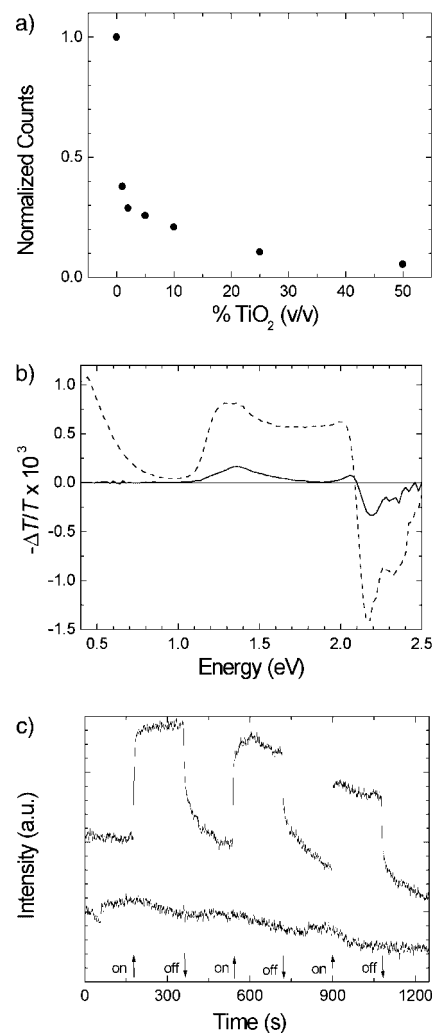

Fig. 2. a) Photoluminescence intensity of MDMO-PPV:TiO$_2$ bulk-heterojunctions with varying amounts of TiO$_2$, (1 %, 2 %, 5 %, 10 %, 25 %, 50 % volume) with excitation at $\lambda = 488$ nm. (The data are corrected for differences in optical density). b) Photoinduced absorption spectra of 1:1 (v/v) MDMO-PPV:TiO$_2$ (dashed line) and 1:1 (v/v) MDMO-PPV:ZrO$_2$ (solid line) bulk-heterojunctions. c) Temporal evolution of the ESR signals during 180 s light-on/light-off modulation of MDMO-PPV:TiO$_2$ (upper) and MDMO-PPV:ZrO$_2$ (lower) bulk-heterojunctions.

The reduction in photoluminescence implies a fast deactivation of the MDMO-PPV singlet excited state. This is supported by time-resolved PL measurements. The major component in the PL decay of a pristine polymer film has a time constant of 300 ± 40 ps. The PL decay kinetics of the bulk-heterojunction contains a major contribution of a lifetime shorter than 10 ps (faster than the resolution of the set-up). The residual emission is ascribed to photoexcitations within the MDMO-PPV phase that do not reach the interfacial area with TiO$_2$.

The photoinduced absorption (PIA) spectrum of the MDMO-PPV:TiO_2 bulk-heterojunction thin film recorded at 80 K with excitation at 488 nm, exhibits two absorptions at 0.42 and 1.32 eV and a bleaching signal at 2.18 eV with a shoulder at 2.32 eV (Fig. 2b, dashed line). The absorption bands at 0.42 and 1.32 eV are assigned to the two dipole-allowed transitions of the radical cation of MDMO-PPV, while the two bleaching signals are attributed to the MDMO-PPV ground state.[17] By changing the modulation frequency and the excitation intensity we find that the decay kinetics of the photogenerated charges follows a bimolecular decay process, consistent with the recombination of positive and negative charges. A broad distribution of lifetimes is found that extends into the millisecond time domain.

Light-induced electron spin resonance (LIESR) measurements also provide evidence of a charge-transfer reaction between MDMO-PPV and TiO_2 (Fig. 2c, upper). Illumination at $\lambda = 496$ nm of a MDMO-PPV:TiO_2 bulk-heterojunction at 130 K results in LIESR signals at $g = 2.0024$, consistent with the formation of MDMO-PPV radicals.[9] The LIESR signal consists of a permanent part and a part that depends on the changing intensity of the excitation beam. The temporal evolution of the ESR signal at $g = 2.0024$ shows the fast rise in signal upon illumination. In the dark, the signal disappears by multiple relaxation mechanisms with time constants longer than 10 s.

To demonstrate unambiguously that the photoinduced charge-transfer reaction occurs between MDMO-PPV and TiO_2, a bulk-heterojunction of MDMO-PPV and ZrO_2 was prepared in a similar way using zirconium(IV) butoxide as a precursor ($Zr(OC_4H_9)_4$). ZrO_2 has similar surface and optical properties as TiO_2 but its conduction band is approximately 1 eV higher in energy than that of TiO_2. Hence, a photoinduced charge-transfer between MDMO-PPV and ZrO_2 is energetically unfavorable. In agreement with this expectation, the PIA spectrum of the MDMO-PPV:ZrO_2 bulk-heterojunction shows a single band at 1.36 eV, which is assigned to the triplet–triplet transition of MDMO-PPV and a ground-state bleaching at 2.20 eV (Fig. 2b, solid line).[9] The LIESR spectrum of a MDMO-PPV:ZrO_2 bulk-heterojunction shows a small permanent photoinduced signal after illumination, which cannot be switched on and off by modulation of the light intensity (Fig. 2c, lower). The permanent signals in both MDMO-PPV:TiO_2 and MDMO-PPV:ZrO_2 samples are attributed to a small degree of irreversible photo-oxidation.

Photovoltaic devices have been prepared by sandwiching the MDMO-PPV:TiO_2 bulk-heterojunction between charge-selective electrodes. ITO/PEDOT:PSS (ITO: indium tin oxide; PSS: poly(styrene sulfonate); PEDOT: poly(3,4-ethylene-dioxythiophene)) is used as transparent high-work-function electrode to collect the holes, and LiF/Al is used as low-work-function electrode for electron collection. The photovoltaic properties of the device are demonstrated by spectral response measurements (Fig. 3a). The spectral response resembles the absorption spectrum of the bulk-heterojunction. For
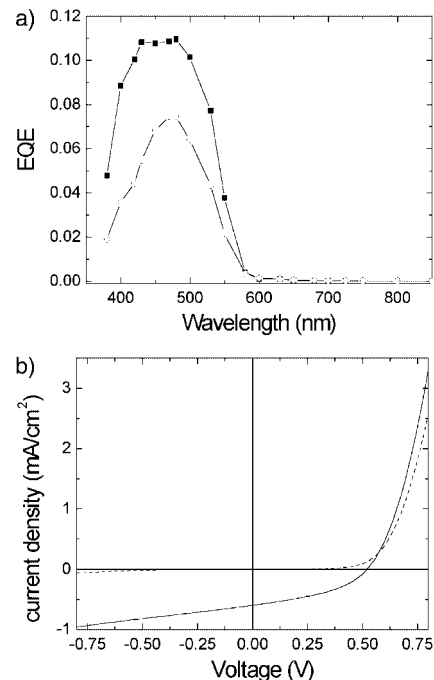

Fig. 3. Photovoltaic properties of ITO/PEDOT-PSS/MDMO-PPV:TiO_2/LiF/Al devices. a) External quantum efficiency of 1:1 (v/v) (open circles) and 4:1 (v/v) (solid squares) bulk-heterojunctions. b) I–V curve in the dark (dashed line) and under illumination (~70 mW cm^{-2}) (solid line) of a 4:1 (v/v) bulk-heterojunction.

a 1:1 (v/v) bulk-heterojunction, a peak external quantum efficiency (EQE) of ca. 7 % is reached. Upon decreasing the fraction of TiO_2 to 20 %, the EQE increases to 11 %. Integration of the measured spectral response of the 4:1 mixture with the AM 1.5 (AM = air mass) solar spectrum affords an estimate for the short-circuit current density (I_{sc}) of 0.87 mA cm^{-2} under AM 1.5 conditions (1000 W m^{-2}). I–V measurements under illumination with a simple halogen lamp, set at roughly 0.7 sun intensity, yields $I_{sc} = 0.6$ mA cm^{-2}, an open-circuit voltage $V_{oc} = 520$ mV, and a fill-factor, $FF = 0.42$ (Fig. 3b). For a similar control device made using MDMO-PPV without any TiO_2, the short-circuit current is negligible (<0.02 mA cm^{-2}), confirming the effectiveness of the bulk-heterojunction.

In conclusion, a new method is presented to prepare hybrid donor–acceptor bulk-heterojunctions based on a p-type polymer and an n-type inorganic semiconductor. Spin-casting of MDMO-PPV and titanium(IV) isopropoxide from solution onto a substrate and conversion in air produces at least 65 % TiO_2, as shown by XPS. Phase separation occurs in nanometer-range dimensions. In these bulk-heterojunctions an efficient photoinduced charge transfer occurs, generating charges with long-lived components, as inferred from PL, PIA, and LIESR spectroscopy. The new hybrid bulk-heterojunction was employed as the active layer in a photovoltaic device using the glass/ITO/PEDOT:PSS/MDMO-PPV:TiO_2/LiF/Al configuration, resulting in a photovoltaic response with an EQE of up to 11 %.

Experimental

Bulk-heterojunctions of MDMO-PPV and TiO_2 were made by spin-casting a solution of MDMO-PPV ($2.5\ mg\,mL^{-1}$) and $Ti(OC_3H_7)_4$ ($40\ \mu L\,mL^{-1}$; for a 1:1 (v/v) ratio) in dry THF on a quartz substrate. To allow $Ti(OC_3H_7)_4$ to react with moisture, the samples were kept in the dark, in air overnight. Then, the samples were left in a dynamic vacuum (10^{-6} mbar) for at least 18 h, to remove any volatile products released in the hydrolysis reaction.

Absorption spectra were recorded on a Perkin–Elmer Lambda 40 spectrometer. Fluorescence spectra were recorded on an Edinburgh Instruments F290 by photoexcitation at 488 nm and recording at 580 nm. Time-correlated single-photon-counting fluorescence studies were performed on an Edinburgh Instruments LifeSpec-PS spectrometer by photoexcitation at 400 nm and recording at 650 nm. Photoinduced absorption spectroscopy was performed using a home-built set-up as described previously [9].

For XPS, photoelectrons were collected at an electron take-off angle of 0° from normal, after excitation of the surface by non-monochromatized Mg Kα radiation. The binding energy shifts due to surface-charging were corrected using the C(1s) level at 285 eV, as an internal standard. The XPS peaks were assumed to have 70 % Gaussian and 30 % Lorentzian line shapes, and were resolved into individual components by a non-linear least-squares procedure after proper subtraction of the baseline.

AFM images were recorded on glass substrates with a Nanoscope Digital D3000 AFM, operating under ambient conditions in tapping mode. Microfabricated silicon cantilevers (FESP) with a spring constant of $1-5\ N\,m^{-1}$ were used.

LIESR spectra were recorded with a Bruker ESP 300 spectrometer for a sample in a dynamic vacuum of 10^{-5} mbar at 130 K. Excitation light was introduced into the microwave cavity utilizing a cw continuous wave argon ion laser beam (496 nm; 65 mW) passing through a 50 % transmission grid.

The photovoltaic devices were prepared by spin-coating EL-grade PEDOT/PSS (Bayer AG) onto pre-cleaned, patterned indium tin oxide on glass substrates (14 $\Omega/\square$). Subsequently, the photoactive layer was deposited. The counter electrode of LiF (1 nm) and aluminum (100 nm) was deposited by vacuum evaporation. Each substrate consists of four cells of 0.1 cm², 0.17 cm², 0.33 cm², and 1.0 cm², respectively, and reproducibility among the cells lies within 20 %.

I–V and spectral-response measurements were carried out under a nitrogen atmosphere, inside a glove-box to prevent photo-oxidation of the polymer. The home-built set-up consists of a 12 V/50 W halogen lamp as light source and a set of 22 interference filters as monochromator. Spectral response measurements were performed without bias illumination, with respect to a calibrated Si solar cell.

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[18] The O(1s) peak at 530.4 eV also contains a component at 531.9 eV, corresponding to O(1s) from Ti–O–H, Ti–O–C, or H_2O originating from adsorption at the surface of the samples or due to residuals from the iso-propoxide. Hence, the ratio O(1s)(Ti–O–Ti)/O(1s)(Ti–O–X; X = C, H; or H_2O adsorption) accounts for the minimum conversion of $Ti(OC_3H_7)_4$ into TiO_2.
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Non-Destructive Readout of the Photochromic Reactions of Diarylethene Derivatives Using Infrared Light**

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Photochromic molecules have attracted much attention from both fundamental and practical points of view because of their potential for applications to optical devices such as optical memories and switches.[1] Among the photochromic compounds, diarylethenes are regarded as the best candidates, because of the thermal stability of both isomers and their fatigue resistance.[2] For practical applications to optical memory, non-destructive read-out capability is indispensable. When the recorded information is read out by light that electronically excites the photochromic compounds the information is lost during the reading process. Several ways to avoid this have been proposed. Typical approaches are i) introduction of long conjugated oligothiophene rings as the aryl groups to provide thermal gated reactivity,[3] ii) use of two laser beams for readout of the recording,[4] iii) dual-mode-type recording systems, which combine two reversible processes that can be addressed by two independent stimuli.[5,6] These methods are based on gated photochromism. Another approach is to use readout light that cannot cause any photoreaction.

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