[70]Fullerene-Based Photovoltaics

Efficient Methano[70]fullerene/MDMO-PPV Bulk Heterojunction Photovoltaic Cells**

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The widespread use of solar cells as a renewable source of energy is seriously held back by the high cost of the existing crystalline silicon-based technology. The prospect of cheap reel-to-reel processing makes organic semiconducting mate-

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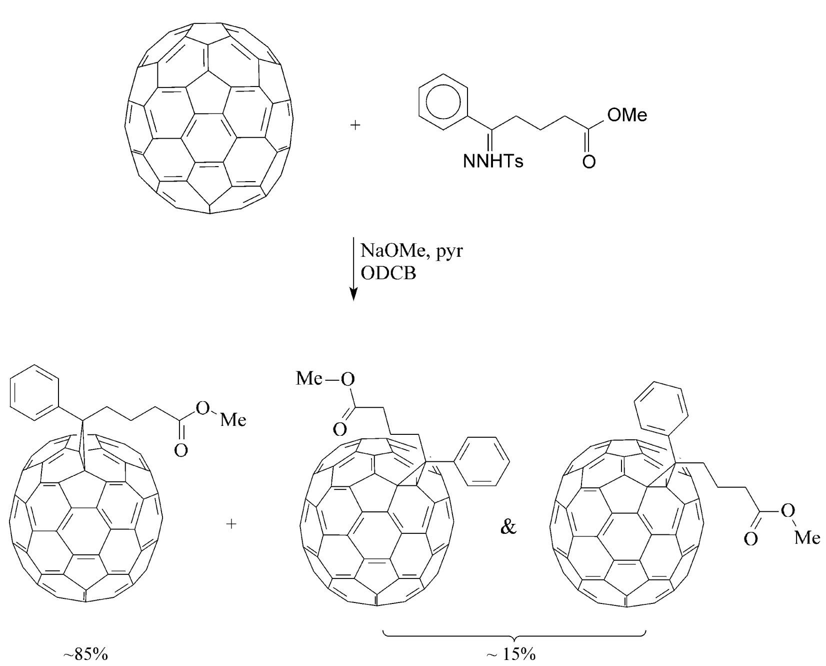
rials interesting alternatives for the future generation of photovoltaic devices.[1–5] Organic solar cells that have received considerable attention are of the so-called polymer/fullerene bulk heterojunction type.[6–8] Until now, the photoactive layer of these devices routinely consists of a mixture of a π-conjugated polymer acting as electron donor, and a soluble [60]fullerene derivative, methano[60]fullerene [6,6]-phenyl C_{61} butyric acid methyl ester ([60]PCBM) as electron acceptor.[9] Optimized internal quantum efficiencies (IQE = fraction of absorbed photons converted to electric current) close to 100 % have been reported,[7] which demonstrates that very efficient charge generation and collection can be achieved. Therefore, the current densities, which are still low compared to inorganic semiconductor devices, are mainly limited by incomplete utilization of the incident light, because of a poor match between the absorption spectrum of the materials and the solar emission spectrum. The polymers only absorb light at wavelengths less than 650 nm, but more importantly, [60]PCBM, which amounts to at least 75 % of the photoactive layer, has a very low absorption coefficient in the visible region of the spectrum. The low absorption of C_{60} derivatives can be attributed to a high degree of symmetry, making the lowest-energy transitions formally dipole forbidden. Therefore, when the C_{60} moiety of [60]PCBM is replaced by a less symmetrical fullerene, these transitions will become allowed and a dramatic increase in light absorption is expected.[10] Herein, we report on a bulk heterojunction photovoltaic cell in which an isomeric mixture of C_{70} derivatives is used as an electron acceptor in combination with poly(2-methoxy-5-{3′,7′-dimethyloctyloxy}-*p*-phenylene vinylene) (MDMO-PPV). [70]PCBM (for instance, in this case a mixture of isomeric [6,6]-phenyl C_{71} butyric acid methyl esters) is the higher fullerene analogue of [60]PCBM, and displays improved light absorption in the visible region. Consequently, when this material is used in a photovoltaic cell instead of [60]PCBM, 50 % higher current densities are obtained. The overall power-conversion efficiency η, measured under standard test conditions (AM1.5 (AM = air mass), 1000 W m^{-2}, 25 °C), amounts to 3.0 %.



Scheme 1. Synthesis of [70]PCBM. At the bottom, the structures of the chiral α-type isomer (left) and the two possible achiral β-type isomers (right). Ts = toluene-4-sulfonyl.

The synthesis of [70]PCBM was performed in an analogous procedure to that described earlier for [60]PCBM (Scheme 1).[9] However, 1,3-dipolar addition to C_{70} leads to a mixture of regioisomers.[11] The ^{1}H NMR spectrum of the monoadduct fraction ("[70]PCBM"), isolated from the higher adducts and unreacted C_{70} by column chromatography, reveals signals for methoxy groups (ratio ≈ 7:85:8) at δ = 3.48, 3.65, and 3.72 ppm, respectively, which indicates the presence of three isomers. Since the ^{13}C NMR spectrum for typical parts of the molecule (i.e., the phenyl ring, the butyric acid, and methyl ester moieties) does not display multiple resonances, it is concluded that the minor isomers are not visible, due to their relatively low concentration. We therefore attribute all visible ^{13}C resonances to the major isomer. More than 60 resonances for the fullerene carbon atoms are observed, clearly indicating the chirality of the isomer. Based on this observation and on the basis of the known reactivity of C_{70}, we conclude that the major isomer is the "α type"[11] compound formed by 1,3-dipolar addition (with subsequent loss of nitrogen with isomerization to [5,6] fulleroid(s), and followed by back-isomerization to the [6,6]methano[70]fullerene) to the most "polar" double bond (the C(8)-C(25) bond),[12] yielding a chiral derivative. Most likely, the two minor isomers are the achiral stereoisomeric "β type" addends, in which the addend is bound to the C(9)-C(10) double bond (the most "polar" C=C bond in the C_{70} skeleton, after the C(8)-C(25) bond).

The UV/Vis absorption of the [70]PCBM mixture is shown in Figure 1, together with that of [60]PCBM. The significantly higher absorption coefficient in the visible region is most relevant for the application in photodiodes, photodetectors, and photovoltaics. The [70]PCBM mixture is readily soluble in common solvents.

The photoinduced electron transfer from dialkoxy-PPV to fullerenes in the solid state that occurs after excitation of the polymer is well documented and was shown to occur within 40 fs.[13,14] From the spectral response[6] of [60]PCBM:MDMO-PPV photovoltaic cells at wavelengths greater than 600 nm, where the fullerene is excited exclusively, it can be inferred that excitation of the fullerene also contributes to the photocurrent generation, but comparatively little is known about this process. For mixed [70]PCBM:MDMO-PPV (4:1, w/w) films, spin coated from chlorobenzene on a quartz substrate, near steady-state photoinduced absorption (PIA) measurements (performed at 80 K in a nitrogen atmosphere) give direct spectral evidence for photoinduced charge separation, not only upon

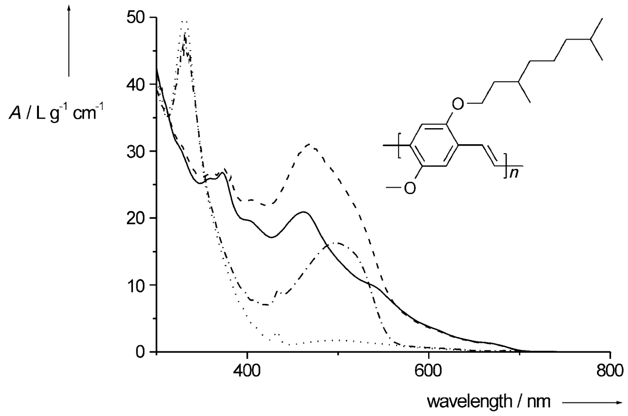


Figure 1. UV/Vis spectra of [70]PCBM (——) and [60]PCBM (•••••), both in toluene. To illustrate the contribution of MDMO-PPV to the absorption, the (normalized) spectra of [70]PCBM:MDMO-PPV (4:1, w/w; -----) and [60]PCBM:MDMO-PPV (4:1, w/w; –•–•), also in toluene, are also represented. The inset shows the structure of MDMO-PPV.

excitation of the polymer, but also after selective excitation of [70]PCBM at 630 nm. The PIA spectra measured after excitation at 488 and 630 nm exactly coincide (Figure 2a), and display two absorptions at 0.40 and 1.35 eV—characteristic for cation radicals on MDMO-PPV—and a bleaching signal at 2.25 eV of the MDMO-PPV ground state. The kinetics of charge generation were examined with pump-probe spectroscopy in the sub-picosecond time domain (Figure 2b) by tracing the intensity of the PIA signal of the high-energy cation radical absorption of the MDMO-PPV at 970 nm (1.28 eV). Excitation at 510 nm results in the rise of this band within 500 fs (resolution of the set-up), consistent with ultrafast measurements reported previously.[13,14] Selective excitation of [70]PCBM in the mixture at 660 nm also leads to a rise time within 500 fs. This demonstrates that photoinduced electron transfer from the MDMO-PPV to [70]PCBM is a sub-picosecond reaction, irrespective of which chromophore is excited.

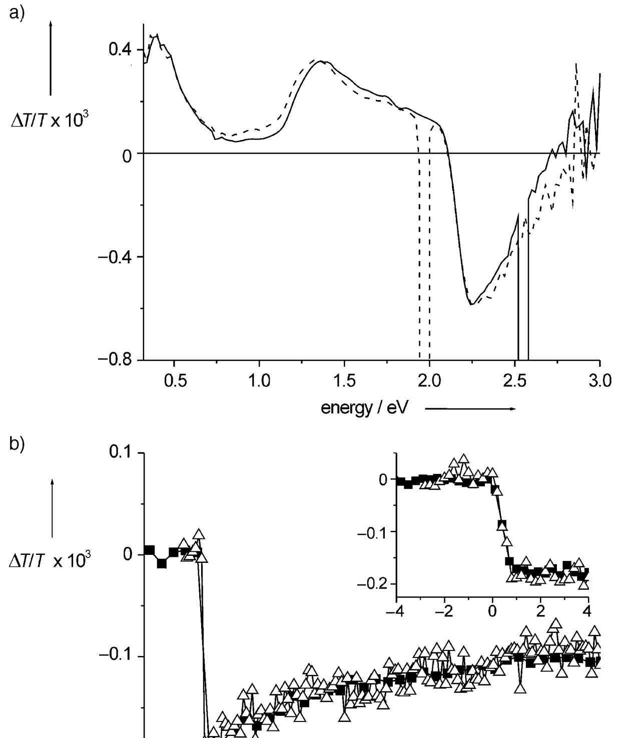


Figure 2. a) Normalized photoinduced absorption spectra of [70]PCBM:MDMO-PPV (4:1 w/w) on quartz after excitation at 488 nm (——) and 630 nm (-----); b) differential transmission dynamics of [70]PCBM:MDMO-PPV (4:1 w/w) on glass after excitation at 510 (△) and 660 nm (■), respectively.

The efficiency of charge generation was examined by steady-state and time-resolved photoluminescence (PL) measurements. Because the ultrafast charge transfer deactivates the excited state before luminescence can occur, a decrease in PL signal of the [70]PCBM:MDMO-PPV mixtures with respect to the pristine materials is expected. As is the case for [60]PCBM:MDMO-PPV mixtures,[15] the MDMO-PPV emission, observed at 570 nm after excitation at 488 nm, is almost completely quenched, which indicates near quantitative charge generation upon polymer excitation. This polymer PL quenching occurs for all [70]PCBM:MDMO-PPV films, spin cast from several different solvents. On the other hand, quenching of the [70]PCBM emission at 720 nm greatly depends on the processing solvent. When chlorobenzene is used, only 30% of the PL is quenched, whereas 60% and over 95% quenching occurs for films from *o*-xylene and *o*-dichlorobenzene (ODCB), respectively. This solvent dependence is also reflected in time-resolved photoluminescence measurements (Figure 3a). The decay kinetics of the fullerene emission at 720 nm of the [70]PCBM:MDMO-PPV (4:1 w/w) mixture, spun from chlorobenzene, hardly differs from that shown by the pristine fullerene. In contrast, for mixtures spin coated from *o*-xylene and especially from ODCB, significantly shorter lifetimes are observed.

The dramatic differences in PL quenching, and the associated charge-generation efficiency is explained by changes in the morphology of the films due to the processing solvent. It has been shown that different solvents can result in distinctly different efficiencies for fullerene:PPV photovoltaic cells as a result of changed morphologies.[6] Tapping-mode atomic force microscopy (AFM) was employed to gain insight into the structure of the different [70]PCBM:MDMO-PPV mixtures. The topography images reveal a very rough surface (root-mean-square (rms) roughness = 12 nm) for films from chlorobenzene and lateral structures with diameters between one and three micrometers, suggesting demixing of the polymer and methano[70]fullerene on a very large scale (Figure 3b). Films from *o*-xylene are smoother (rms roughness = 7 nm) and the apparent domains somewhat smaller but only the films from ODCB are really smooth (rms roughness = 1 nm) with lateral features well under one micrometer.

The very coarse demixing observed by AFM explains the poor PL quenching of the [70]PCBM:MDMO-PPV films processed from chlorobenzene and *o*-xylene. When pure

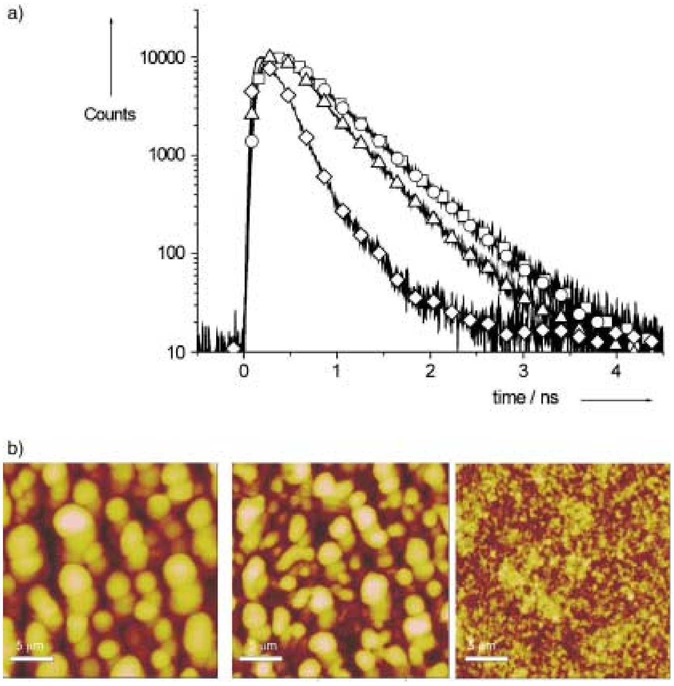


Figure 3. a) Photoluminescence decay of the fullerene emission of [70]PCBM:MDMO-PPV (4:1 w/w) blends at 720 nm on glass, spin coated from chlorobenzene (○), *o*-xylene (△), and ODCB (◇). The PL decay of a pristine [70]PCBM film (□) is also shown; b) AFM tapping-mode height images of [70]PCBM:MDMO-PPV (4:1 w/w) blends on glass, spin coated from chlorobenzene (left, *z* range = 86 nm, rms roughness = 12 nm), *o*-xylene (center, *z* range = 37 nm, rms roughness = 7 nm), and ODCB (right, *z* range = 8.2 nm, rms roughness = 1.0 nm).

methanofullerene phases are present with a radius larger than the exciton diffusion length, part of the excitons do not reach the fullerene/polymer interface. Consequently, charge transfer cannot occur and the excitation will decay (partly) radiatively. The observation that the MDMO-PPV emission is completely quenched, irrespective of the processing solvent, suggests that in all cases some fullerene is present in the polymer-rich phase, which deactivates the MDMO-PPV excited state.

The large solvent-induced morphology differences are also reflected by the photovoltaic behavior of the [70]PCBM:MDMO-PPV films. Photovoltaic cells were made by sandwiching the photoactive mixture, consisting of [70]PCBM and MDMO-PPV in a 4.6:1 (w/w) ratio,[16] between charge-selective electrodes. ITO/PEDOT:PSS (ITO: indium tin oxide; PEDOT: poly(3,4-ethylenedioxythiophene; PSS: poly(styrene sulfonate) was used as a transparent, high-work-function electrode to collect the holes, and LiF/Al[17,18] as low-work-function electrode for electron collection. The external quantum efficiency (EQE; that is, the fraction of incident photons converted into electric current) of a device spin-coated from chlorobenzene does not exceed 0.2 (Figure 4a), and thus remains much lower than the EQE of corresponding [60]PCBM:MDMO-PPV cells (usually between 0.5–0.55). This can be rationalized by the incomplete charge generation after [70]PCBM excitation that result from the large methano[70]fullerene domains. On the other hand, the EQE of a photovoltaic device processed from ODCB is much higher, with a maximum value of 0.66 at 480 nm. This value is higher than that of an optimized [60]PCBM:MDMO-PPV cell and, as a result of the increased absorption by [70]PCBM, the spectral response is significantly broader as well. Integration of this spectral response with the tabulated AM1.5G spectrum, normalized to 1000 W m^{-2}, renders an expected value of 7.9 mA cm^{-2} for the short-circuit current (I_{sc}) under illumination with the solar spectrum. This value corresponds very well to the I_{sc} = 7.6 mA cm^{-2} obtained by current–voltage measurements (Figure 4b) carried out under a solar simulator according to standard test conditions (AM1.5, 1000 W m^{-2}; 25 °C; correction for spectral mismatch[19]). A value of I_{sc} = 7.6 mA cm^{-2} for the [70]PCBM:MDMO-PPV devices means an increase of over 50 % with respect to an optimized [60]PCBM:MDMO-PPV cell. On the other hand, the open-circuit voltage V_{oc} of 0.77 V and a fill factor (*FF*) of 0.51 are somewhat lower for the [70]PCBM:MDMO-PPV devices,[20] resulting in an overall power-conversion efficiency (η) of 3.0 %.

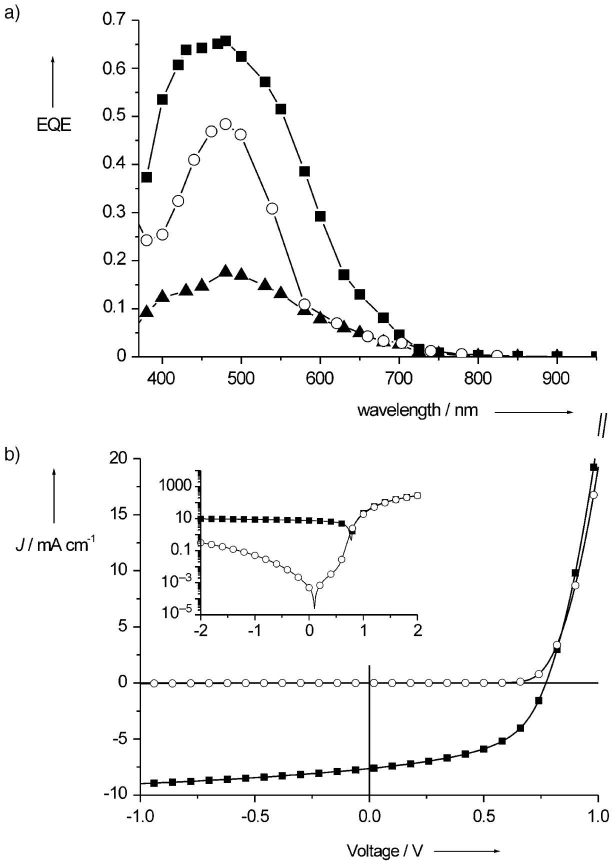


Figure 4. Photovoltaic properties of an ITO/PEDOT-PSS/fullerene:MDMO-PPV/LiF/Al device with an active area of 0.1 cm^2. a) External quantum efficiency (EQE) of [70]PCBM:MDMO-PPV cells, spin coated from chlorobenzene (▲) and ODCB (■), and of [60]PCBM:MDMO-PPV devices spin coated from chlorobenzene (○); b) current–voltage characteristics of [70]PCBM:MDMO-PPV devices, spin coated from ODCB, in the dark (○) and under illumination (AM1.5, 1000 W m^{-2}; ■). The inset shows the dark and illuminated *I*/*V* curves in a semilogarithmic plot.

Experimental Section

MDMO-PPV and [70]PCBM were synthesized according to known procedures.[9,21] Details about the [70]PCBM synthesis and characterization are given in the Supporting Information.

Absorption spectra were recorded on a PerkinElmer Lambda 40 spectrometer. Near-steady-state and sub-picosecond transient photoinduced absorption spectroscopy measurements were performed using equipment described previously.[22] Fluorescence spectra were recorded on an Edinburgh Instruments F920. Time-correlated single-photon-counting fluorescence studies were performed on an Edinburgh Instruments LifeSpec-PS spectrometer by photoexcitation at 400 nm and recording at 720 nm. AFM images were recorded on glass substrates with a Nanoscope Digital D3000 AFM operating under ambient conditions in tapping mode. Microfabricated silicon cantilevers (FESP) were used with a spring constant of 1–5 $N m^{-1}$.

The photovoltaic devices were prepared by spin coating EL-grade PEDOT:PSS (Bayer AG) onto pre-cleaned, patterned indium tin oxide substrates (14 Ω per square). The photoactive layer was deposited by spin coating from the appropriate solvent. The counterelectrode of LiF (1 nm) and aluminum (100 nm) was deposited by vacuum evaporation at 10^{-6} mbar. The active area of the cell was 0.1 cm^2.

Spectral response measurements were performed using a 12 V/50 W halogen lamp as light source and 22 interference filters as a monochromator. Measurements were carried out without bias illumination with respect to a calibrated Si solar cell. The experiments were carried out in a nitrogen-filled glove box to prevent degradation of the device by water or oxygen, which is commonly observed for polymer devices. Current voltage measurements were performed on devices encapsulated by araldite (Ciba)/aluminum foil under a Spectrolab ZT-10 solar simulator outside the glove box, using a Keithley SMU 2400 source meter. A polycrystalline silicon solar cell, calibrated at PTB, Braunschweig (Germany), was used as reference cell. Efficiencies were determined according to international standard norms (ASTM, IEC).[23]

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[1] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, *270*, 1789–1791.

[2] W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, *Science* **2002**, *295*, 2425–2427.

[3] P. Peumans, S. R. Forrest, *Appl. Phys. Lett.* **2001**, *79*, 126–128.

[4] M. Gangstrom, K. Petrisch, A. C. Arias, A. Lux, M. R. Andersson, R. H. Friend, *Nature* **1998**, *395*, 257–260.

[5] J. Nelson, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 87–95.

[6] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, *Appl. Phys. Lett.* **2001**, *78*, 841–843.

[7] P. Schilinsky, C. Waldauf, C. J. Brabec, *Appl. Phys. Lett.* **2002**, *81*, 3885–3887.

[8] F. Padinger, R. S. Rittberger, N. S. Sariciftci, *Adv. Funct. Mater.* **2003**, *13*, 85–88.

[9] J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao, C. L. Wilkins, *J. Org. Chem.* **1995**, *60*, 532–538.

[10] J. W. Arbogast, C. S. Foote, *J. Am. Chem. Soc.* **1991**, *113*, 8886–8889.

[11] For a review on the reactivity of C_{70}, see: C. Thilgen, F. Diederich, *Top. Curr. Chem.* **1999**, *199*, 135–171.

[12] W. H. Powell, F. Cozzi, G. P. Moss, C. Thilgen, R. J.-R. Hwu, A. Yerin, *Pure Appl. Chem.* **2002**, *74*, 629–695. The IUPAC name for the major [70]PCBM isomer is: methyl 5-(3′*H*-cyclopropa[8,25](C70-*D*5h(6))[5,6]fullerenyl)-5-phenylpentanoate.

[13] C. J. Brabec, G. Zerza, G. Cerullo, S. De Sivestri, S. Luzatti, J. C. Hummelen, S. N. Sariciftci, *Chem. Phys. Lett.* **2001**, *340*, 232–236.

[14] B. Kraabel, D. McBranch, N. S. Sariciftci, D. Moses, A. J. Heeger, *Phys. Rev. B* **1994**, *50*, 18543–18552.

[15] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, *Science* **1992**, *258*, 1474–1475.

[16] Photovoltaic cells were prepared with different [70]PCBM:MDMO-PPV weight ratios, ranging from 2:1 to 5:1.

[17] C. J. Brabec, S. E. Shaheen, C. Winder, N. S. Sariciftci, P. Denk, *Appl. Phys. Lett.* **2002**, *80*, 1288–1290.

[18] L. S. Hung, C. W. Tang, M. G. Mason, *Appl. Phys. Lett.* **1997**, *70*, 152–155.

[19] J. M. Kroon, M. M. Wienk, W. J. H. Verhees, J. C. Hummelen, *Thin Solid Films* **2002**, *403–404*, 223–228.

[20] A lower value of V_{oc} may be due to a lower reduction potential of the electron acceptor: C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, J. C. Hummelen, *Adv. Funct. Mater.* **2001**, *11*, 374–380. However, the reduction potentials of [60]PCBM and [70]PCBM are identical (not shown). Therefore, we attribute the reduced V_{oc} value to recombination losses. The lower *FF* value is related to a higher series resistance over the device.

[21] F. Louwet, D. Vanderzande, J. Gelan, J. Mullens, *Macromolecules* **1995**, *28*, 1330–1331.

[22] P. A. Van Hal, E. H. A. Beckers, S. C. J. Meskers, R. A. J. Janssen, B. Jousselme, P. Blanchard, J. Roncali, *Chem. Eur. J.* **2002**, *8*, 5415–5429.

[23] P. M. Sommeling, H. C. Rieffe, J. A. M. Van Roosmalen, A. Schönecker, J. M. Kroon, J. A. Wienke, A. Hinsch, *Sol. Energy Mater. Sol. Cells* **2000**, *62*, 399–410.