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Kelvin Probe Force Microscopy Study of Conjugated Polymer/Fullerene Organic Solar Cells

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We conducted a comprehensive Kelvin probe force microscopy (KPFM) study of the “classical” organic solar cell system consisting of the MDMO-PPV:PCBM blend. The KPFM method yields detailed information of topography and local work function on the nanometer scale. Experiments were performed either in the dark or under laser illumination to extract locally resolved surface photovoltage. We identified distinct differences in energetics on the surface of chlorobenzene- and toluene-cast blend films. The electronic and structural behavior of the toluene-cast blend films were analyzed in relation to illumination and substrate temperature. Together with previous studies we were able to interpret the KPFM results and draw some conclusions regarding the correlation between the nanostructural properties and photovoltaic performance of organic solar cells. [DOI: 10.1143/JJAP.44.5370]

KEYWORDS: Kelvin probe force microscopy, organic solar cells, surface photovoltage, MDMO-PPV, PCBM

1. Introduction

In the field of plastic electronics, there has been an increasing interest over the last years in the development of organic solar cells.^{1–9)} Low weight, flexibility, and predicted low manufacturing costs are the main stimulating factors for research in this area, opening a variety of technological possibilities (*e.g.* indoor, automotive and mobile applications). The numerous possibilities of synthesizing new organic materials with tuned electro-optical properties enhance the creative involvement of polymer scientists in this interdisciplinary research. One of the most promising device structures is the concept of a bulk heterojunction organic solar cell. The majority of investigated devices are based on a soluble fullerene derivative 1-(3-methoxycarbonyl) propyl-1-phenyl [6,6]C₆₀ (PCBM) as an electron acceptor and poly-[2-(3,7-dimethyloctyloxy)-5-methyloxy]-para-phenylene-vinylene (MDMO-PPV) as a donor (Fig. 1).

Compared with inorganic devices, overall power conversion efficiencies under normalized solar conditions of bulk heterojunction organic solar cells are low. The highest efficiency of about 3.5% was reported,^{10–12)} and recently, the critical 5% efficiency benchmark seems to have been overcome.¹³⁾ Despite the high external quantum efficiencies ($\approx 80\%$)¹⁴⁾ observed to date, the spectral mismatch of organic absorbers to the solar spectrum results in small

photocurrents. Most of the organic semiconductors investigated today absorb in the visible range, while the sun has its maximum photon density at approximately 700 nm. Furthermore, a certain intrinsic durability of the organic compounds is limiting the efficiency of solar cells: when electrons are excited to higher orbitals, anti-bonding states are occupied and the probability of the decomposition of a compound increases.

Finally, effective light collecting in a blend photovoltaic device demands efficient charge separation and transport. First, the energy bands of the two compounds have to cascade in order to guarantee charge generation after photoexcitation. Second, each compound must provide a continuous path for the transport of separated charge to the contacts. This demands a highly complex morphology between the two compounds with interconnected domains on the nanometer scale to prevent trapping and more ordered regions on the tens of nm scale to guarantee efficient transport channels.

The aim of this study is to clarify the dependence of device power conversion efficiency on the basis of the nanomorphology of MDMO-PPV:PCBM heterojunction organic solar cells by Kelvin probe force microscopy (KPFM). One method of varying the nanomorphology and obtaining reproducible efficiency is changing the spin casting solvent from toluene to chlorobenzene.¹⁵⁾ Detailed studies of devices revealed a finer intermixing of the polymer and fullerene constituents when spin-cast from chlorobenzene solution.^{16–19)} In this study, we compare this two blends by KPFM in ultrahigh vacuum (UHV) to obtain electrical and structural information on the nanoscale. KPFM results show clear differences in the electronic work function (Φ) for different morphologies, indicating low photoactivity of toluene-cast samples.

2. Experimental

UHV-KPFM measurements in this study were conducted by modified Omicron UHV-STM/AFM (pressure $p < 10^{-10}$ mbar).^{20–22)} The topography was determined using the standard frequency modulation technique at the first resonance frequency of the cantilever (≈ 70 kHz). Amplitude modulation detection at the cantilever's second resonance

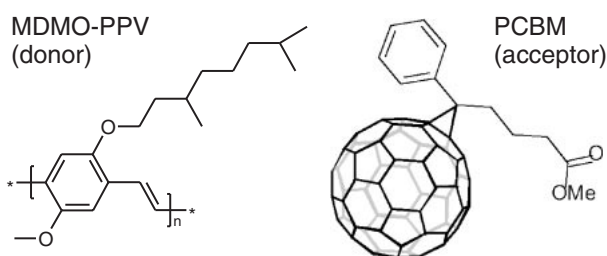


Fig. 1. Molecular structures for MDMO-PPV and PCBM.

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frequency (≈ 420 kHz) with an ac-bias amplitude as small as 100 mV_{pp} enables simultaneous imaging of the contact potential (CP), which is compensated by applying the appropriate voltage to a sample.²³⁾ Further details on UHV-KPFM can be found elsewhere.²⁴⁾ For all measurements PtIr-coated Si cantilevers ($\Phi = 4.28 \pm 0.07$ eV) were used. For the calculation of the absolute work function, each cantilever was calibrated on highly oriented pyrolytic graphite (HOPG) before and after each set of measurements. To determine the surface photovoltage (SPV) of samples, i.e., the change in the work function with illumination ($\Phi_{\text{illuminated}} - \Phi_{\text{dark}}$), the samples were illuminated with a laser diode (wavelength $\lambda = 675$ nm) or a HeCd cw-laser ($\lambda = 442$ nm), both at an intensity of $\approx 70\text{ mW/cm}^2$. All other measurements were performed under dark conditions. The spot width of the AFM detection laser (wavelength $\lambda = 975$ nm) was approximately $20\text{ }\mu\text{m}$, and the laser is effectively withheld from illuminating the sample by the cantilever; therefore has a negligible effect on measurement results.

The solution of MDMO-PPV:PCBM 1 : 4 (1.25 wt. %) was stirred overnight at slightly elevated (50°C) temperatures, without any sonication or filtering. Films were produced by spin-casting from toluene and chlorobenzene at 1500 rpm onto precleaned ITO glass, obtaining a thickness of typically 100 nm. All steps in the production of the films were performed inside an argon glove box in order to prevent any oxygen or water contamination. All samples were sealed inside the glove box during transport. Again under argon atmosphere the samples were loaded into the magazine of the UHV-system and transferred into the vacuum without allowing any air to enter.

3. Results and Discussion

We compared the following two samples. The toluene-cast MDMO-PPV:PCBM blend normally yields a power conversion efficiency of less than $\eta \leq 1\%$ in solar cells and the chlorobenzene-cast blend has a strong intermixing within films and a high efficiency ($\eta < 3\%$).

3.1 Chlorobenzene-cast blend

In Fig. 2 the KPFM measurement of the as-prepared chlorobenzene-cast blend is shown. The topography shown in Fig. 2(a) reveals only height variations in the range of 15 nm with particle sizes of about 50–80 nm. The work function in the dark [Fig. 2(b)] was determined to be $\Phi_{\text{dark}} = 4.55 \pm 0.06$ eV. Figure 2(c) shows the work function under cw-laser illumination measured at nearly the same

position as in the dark. The mean work function shifted towards lower values and was determined to be $\Phi_{\text{illuminated}} = 4.22 \pm 0.06$ eV. For illumination with the laser diode, comparable values were obtained.

The measurements confirm that the blend cast with chlorobenzene had a very homogeneous morphology as well as a uniformly distributed surface potential. The negative shift of the work function under illumination $\text{SPV} = -330\text{ mV}$ results from an accumulation of negatively charged carriers at the surface. That is, due to the illumination, the excitons within the photoactive layer of organic solar cells separate, and free carriers transferred effectively towards the back contact and the surface.

3.2 Toluene-cast blend

Figure 3(a) shows the surface morphology and Fig. 3(b) the simultaneously measured work function of a MDMO-PPV:PCBM film spin-cast from toluene solution in the dark

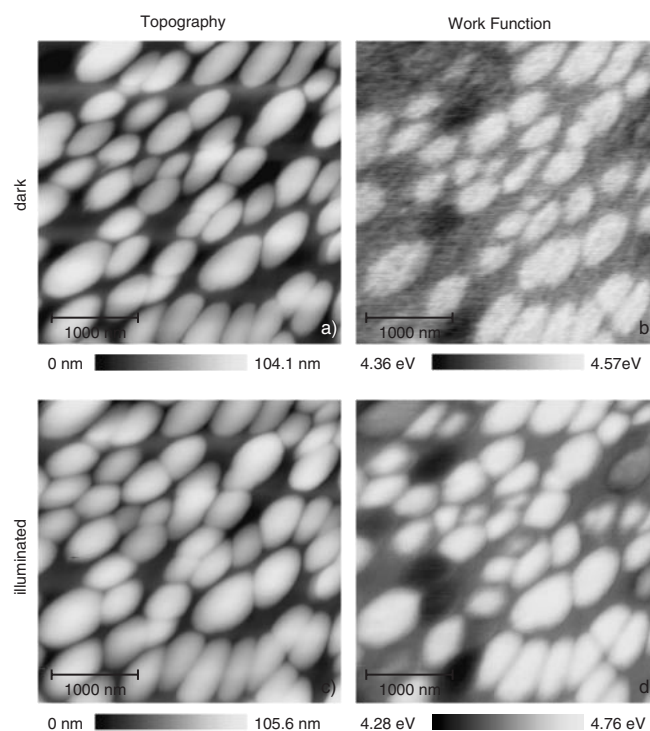


Fig. 3. Topography (a,c) and work function Φ (b,d) of toluene-cast blend film of MDMO-PPV:PCBM at mass ratio of 1 : 4. Measured in the dark (a,b) and under 675 nm laser illumination (c,d). Note that some of the topographical hills produce dark areas and thus low work functions, whereas the majority of the hills produce bright areas with high work functions.

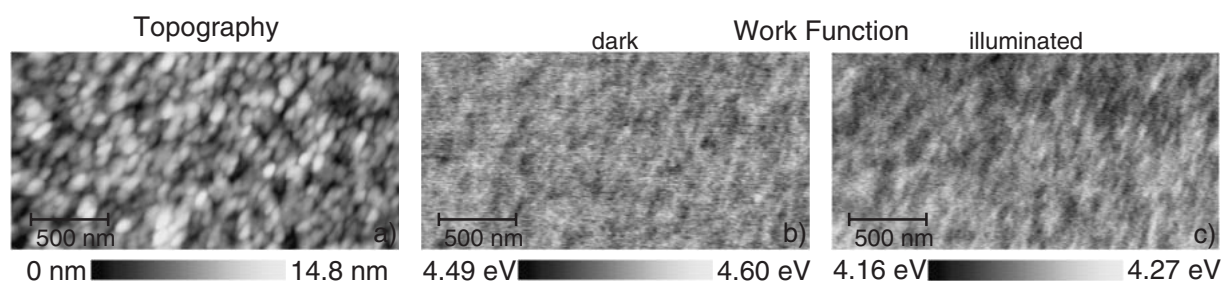


Fig. 2. Topography (a) and work function Φ (b,c) of chlorobenzene-cast blend film of MDMO-PPV:PCBM at mass ratio of 1 : 4, measured in the dark (a,b) and under 442 nm cw-laser illumination (c).

measured by KPFM. The topography reveals hills with a height of about 100 nm and dimensions of 500–800 nm on an otherwise smooth background. In the corresponding work function image [Fig. 3(b)], it can be observed that most of the hills show a work function of $\Phi = 4.51 \pm 0.04$ eV that is higher than the background, $\Phi = 4.43 \pm 0.04$ eV. However, hills that have the same or even a lower work function of $\Phi = 4.39 \pm 0.05$ eV are found. Under illumination with a 675 nm laser diode at nearly the same position [Figs. 3(c) and 3(d)], the mean work function increases. The majority of the hills shows a work function of $\Phi = 4.66 \pm 0.05$ eV, the background $\Phi = 4.46 \pm 0.05$ eV, and the hills that showed before the lowest values still have $\Phi = 4.35 \pm 0.04$ eV. Furthermore, it should be noted, that some of the hills that have shown before work function comparable to the background now have either slightly higher or even lower values.

In Fig. 4 the calculated SPV of this measurement is shown on top of the work function image of the illuminated sample [Fig. 3(d)]. A positive SPV with a maximum of 220 mV is found only on top of the hills that showed before the highest work function values. Whereas a negative SPV is only found in regions with the lowest work function values. The background shows almost no change in work function under illumination.

A combined transmission electron and atomic force microscopy study revealed, that the observed hills are composed of PCBM-rich domains that are found to be embedded in a matrix that consists of a mixture of MDMO-PPV and PCBM.¹⁶⁾ Furthermore, Martens *et al.* found in a KPFM study under ambient conditions a reduction in work function on a single PCBM cluster in comparison to the surrounding matrix.²⁵⁾ The results are explained by the hypothesis that PCBM is, in comparison with MDMO-PPV,

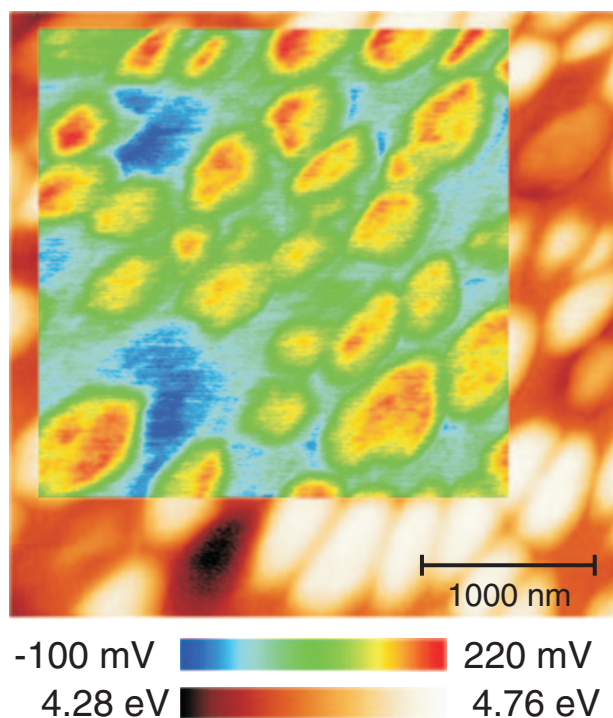


Fig. 4. Locally resolved surface photovoltage (SPV) of toluene-cast film calculated as difference in work function shown in Figs. 3(b) and 3(d). The image in the background represents the work function image under illumination.

a good electron conductor and a less effective hole conductor. Therefore, the PCBM clusters should have a reduced work function under illumination. Very recently, Hoppe and coworkers reported their findings of scanning electron microscopy analysis and mentioned the connection between the presence of a skin layer, surrounding even pure PCBM clusters in toluene-cast films, and different work function values measured by KPFM.^{18,19)}

The comprehensive KPFM and SPV analysis (cf. Figs. 3 and 4) presented here confirms the previous results and provides an explanation for the observed effects in more detail. As can be noted in the work function images of the toluene-cast film, the matrix, that is the area between the PCBM clusters, has a nearly homogeneous distribution of the work function, which is not changed under illumination. From cross-sectional SEM measurements^{18,19)} of the same samples, it was determined that the ITO substrate was completely covered. Therefore, it is very likely that the matrix was mainly build up by MDMO-PPV, as compared with the chlorobenzene-cast films [Fig. 2], in which a 4 : 1 blend of PCBM and MDMO-PPV produced a negative SPV.

The PCBM domains showing a lower work function and a negative SPV are clusters that are not covered by the matrix. Under illumination, excitons are formed at the PCBM/MDMO-PPV interface between the cluster and the surrounding matrix, and charges are separated (photoinduced charge transfer²⁶⁾), which results in an accumulation of electrons within the PCBM and therefore in a lower work function near the cluster surface.

In the case of the high-work-function hills, it is most likely that they are covered by the matrix or even bare MDMO-PPV. The thickness and/or the composition of the skin-layer is influencing the work function and SPV. A higher work function under illumination, which is the case for the majority of the observed clusters, is observed for a skin layer build up mainly from MDMO-PPV. Under illumination charges separate and holes accumulate within the donor-type skin layer. This results in a positive SPV of the hills. With increasing skin layer thickness, the PCBM concentration within this layer increases and the amount of accumulated holes decreases. The work function of the hills adapt to that of the surrounding matrix.

This explanation is also supported by the observed surface condition after annealing the sample in UHV at 150°C for about 4 h. As shown by a previous study by Hoppe *et al.*,¹⁸⁾ under this treatment PCBM-containing clusters form and evolve into microstructures, i.e., crystalline aggregates and some residual circular holes. Figures 5(a) and 5(b) show the topography and the work function of the annealed toluene-cast sample, respectively. The measurement shows that the formed crystalline aggregates have a lower work function than the remaining matrix. This is consistent with the finding that the free PCBM surface has a lower work function than the matrix. Furthermore, under illumination the work function of the PCBM-containing crystalline aggregates decreases (not shown), whereas a slightly positive SPV was obtained within the region of the matrix.

4. Conclusions

The nanoscale morphology as well as the work function within the photoactive blends of conjugated polymers and

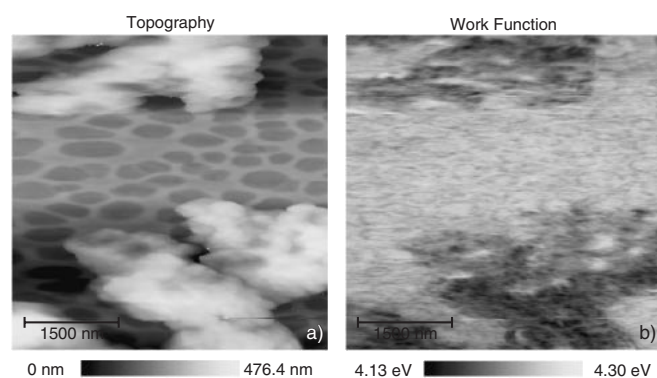


Fig. 5. Topography (a) and work function Φ (b) of a toluene-cast blend film of MDMO-PPV:PCBM with a mass ratio of 1 : 4 measured in the dark after annealing in UHV for 4 h at 150°C.

fullerenes has been investigated by UHV-KPFM. In combination with locally resolved SPV measurements as well as annealing studies, the distribution of PCBM and MDMO-PPV in chlorobenzene- and toluene-cast films was identified and explained in detail. It was proven that when cast from chlorobenzene, the matrix contains a higher PCBM concentration than that cast from toluene. Furthermore, the observed PCBM clusters in the toluene-cast film are either covered by the surrounding matrix or uncovered, which results in a different photovoltaic behavior. Due to the demonstrated correlation between photovoltaic activity and nanostructural properties, KPFM studies will be one key technique for improving the understanding of the link of this properties to photovoltaic performance, and future work will be focussed on this.

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