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Morphology and fluorescence quenching in photovoltaic samples containing fullerene and poly(*p*-phenylene-vinylene) derivatives

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Abstract

We have studied the morphology of different heterogeneous samples containing poly[2-methoxy,5-(3′,7′-dimethyl-octyloxy)]-*p*-phenylene-vinylene (MDMO-PPV) and either fullerene (C_{60}) or 6,6-phenyl C_{61}-butyric acid methyl ester (PCBM) using atomic force microscopy in the shear force detection mode or pulsed-force mode and near-field scanning optical microscopy. These investigations confirm the large influence of preparation conditions on the morphology. Systematic variation of the layer thicknesses in two-layer samples indicate that fluoresecence quenching is restricted to an interface layer with a thickness of about 40 nm.

Keywords: Photovoltaics; Bulk heterojunction solar cells; Fluorescence quenching; Atomic force microscopy; Near-field scanning optical microscopy

1. Introduction

Organic solar cells have been extensively studied during the last decade. Essentially, there are two different types of organic photovoltaic cells, namely the dye-sensitized solar cell [1,2] containing TiO_2 particles covered with metal organic dyes, and organic heterojunction solar cells containing an electron-donating and an electron-accepting organic compound [3]. Among the latter systems, the combination of fullerene (C_{60}) and poly(*p*-phenylene-vinylene) (PPV) derivatives have found to be particularly effective [4], because of an extremely fast electron transfer between these two types of compounds [5]. In addition to the electronic properties of the compounds, the morphology is extremely important for high efficiencies [6,7]. Interpenetrating networks of the electron-donating and the electron-accepting compound (also referred to as bulk heterojunction materials) are most suitable to provide a large power conversion efficiency, and have been used to develop plastic solar cells [8,9].

Heterojunction solar cells consist of an active organic layer sandwiched between two flat electrodes with different work function. At least one electrode must be transparent. Typically, it is made of indium tin oxide (ITO). The efficiency of the photovoltaic effect depends on several steps of the photo-induced charge separation. The incident light needs to be absorbed very efficiently with the organic material in order to excite the electron donor. The transport of the exciton to the donor/acceptor interface and the charge transfer at the interface must be sufficiently fast with respect to the exciton lifetime. Thus, the fluorescence is quenched in suitable systems. Finally, the charge transport to the electrodes must be sufficiently short to avoid recombination of the charges within the organic material. Essentially, the efficiency is limited because the optimum parameters for these different effects compete with each other. For example, effective light absorption is favored by a large layer thickness (>100 nm). On the other hand, the layers should be as thin as possible with respect to the charge transport to the electrodes. A very important parameter is the exciton diffusion length (≈10 nm). Its value limits the occurrence of the charge transfer process to a very narrow region at the organic donor/acceptor interface. Probably, it is due to these limiting effects that the interpenetrating networks are superior to flat layer systems, because the former systems can possess a large interface, very thin coherent regions, and a reasonable total thickness of the organic layer, at the same time.

Interpenetrating networks are usually the result of a phase separation process which occurs during the preparation by spin-coating. The morphology of these non-equilibrium structures is very sensitive to processing conditions. In particular, the typical domain size depends crucially on

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the choice of the solvent [9]. For blends of a conjugated polymer and a fullerene derivative, the power conversion efficiency under AM 1.5 illumination could be enhanced up to 2.5% by choosing the appropriate solvent [10]. Also, interpenetrating networks of a hexabenzocoronene derivative and a perylene compound show a much larger efficiency than samples containing two flat layers consisting of the same materials [11]. Near-field scanning optical microscopy (NSOM) proved to be a suitable tool to investigate both the morphology of polymer blends and their luminescent properties [12].

The aim of the present study is to relate the luminescent properties of interpenetrating networks of a PPV and a fullerene derivative to the morphology of the respective sample. The lateral structure of the systems is studied by investigating the topography and the fluorescence intensity by means of atomic force microscopy (AFM) and near-field scanning optical microscopy, respectively. In order to study the third dimension, we investigated the relative fluorescence intensity as a function of the layer thicknesses in a two-layer system composed of two flat layers of the same material.

2. Experimental

We report investigations on the morphology and the luminescent properties of systems containing poly[2-methoxy,5-(3′,7′-dimethyl-octyloxy)]-*p*-phenylene-vinylene (MDMO-PPV) and either fullerene (C_{60}) or 6,6-phenyl C_{61}-butyric acid methyl ester (PCBM). The samples for the scanning probe microscopy were prepared by spin-coating using a respective mixture of the two compounds in either toluene or chlorobenzene. The ratio between MDMO-PPV and PCBM was always 1:4 (w/w). The concentration of MDMO-PPV was about 0.5 wt.%. The surface of the glass substrates was cleaned by oxygen plasma treatment. Spin-coating ($17\,s^{-1}$) resulted in flat films with uniform thickness of about 80 nm.

Investigations were performed with scanning probe microscopes (model Aurora, Topometrix or model Alpha, WiTec, respectively). The Aurora instrument uses tapered optical fibers for near-field illumination. The distance between the sample surface and the fiber tip is controlled by a feed back loop, using a tuning fork for shear force detection. The fibers were prepared using a fiber puller (model S 2000, Sutter Instruments). The aperture at the respective fiber tip is formed by a shadow evaporation technique applied when the probe is coated with aluminum. All fiber tips were tested using the well-known Fischer mask [13]. Only probes with an optical resolution better than 100 nm were used. The Alpha instrument makes use of cantilevers. The bending of the cantilever is optically detected in order to control either the interaction force or the distance between the cantilever tip and the sample surface. This instrument was operating in four modes: (1) contact atomic force microscopy; (2) pulsed-force mode AFM [14]; (3) confocal scanning microscopy; or (4) near-field optical fluorescence excitation. For the AFM investigations, we used silicon cantilevers (Pointprobe^{TM}-FM from Nanosensors). For optical near-field investigations, cantilevers equipped with a silica tip [15] are applied. The light of luminescence is collected with a microscope lens behind the sample and detected with an avalanche photodiode. The radiation of excitation was blocked by means of an edge filter.In order to investigate the interface of two flat films of the electron-donating and the electron-accepting compound, the first layer (MDMO-PPV) was deposited on a glass substrate by spin-coating. A part of the area of the resulting organic film was covered with the second compound (PCBM) by means of thermal evaporation in high vacuum (10^{-3} Pa). The fluorescence intensity of this layer structure was measured in the confocal configuration of the Alpha microscope. In this case, samples were illuminated through the glass substrate with an Ar ion laser (488 nm), and the luminescence was observed in reflection geometry. Reported relative intensities correspond to the ratio between the fluorescence intensity of the MDMO-PPV covered with PCBM and the fluorescence intensity of the single MDMO-PPV film.

3. Results and discussion

Preliminary studies on the model system MDMO-PPV/poly(methyl methacrylate) (PMMA) demonstrate the capability of the near-field fluorescence technique to identify the domains of the PPV derivative (Fig. 1). The two polymers form a heterogeneous blend where the PPV domains show a

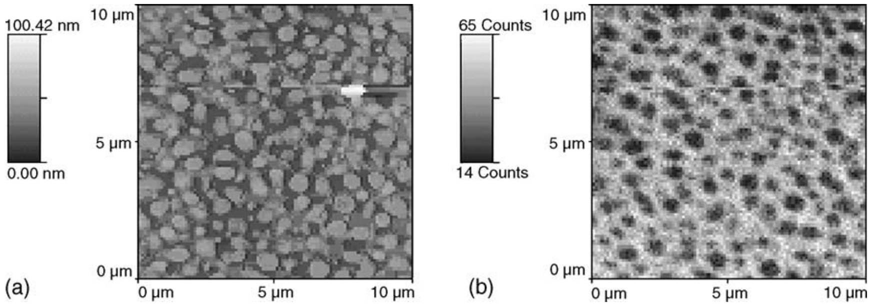


Fig. 1. Topography (a) and fluorescence intensity (b) of a polymer blend consisting of poly(methyl methacrylate) and poly[2-methoxy,5-(3′,7′-dimethyl-octyloxy)]-*p*-phenylene-vinylene.

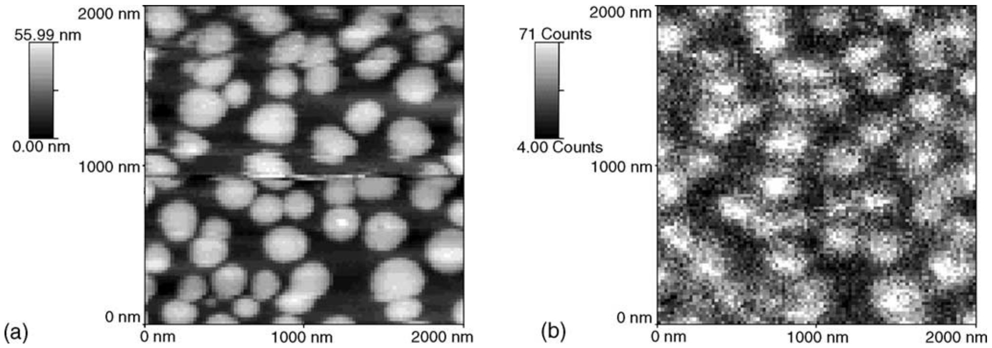


Fig. 2. Topography (a) and fluorescence intensity (b) of a polymer blend consisting of MDMO-PPV and 6,6-phenyl C_{61}-butyric acid methyl ester. This sample was obtained by spin-coating from a solution in toluene.

bright luminescence whereas the islands of PMMA appear dark. The topography (Fig. 1a) is characterized by islands with a lateral size of 150–500 nm which differ in height from their surrounding by about 5 nm. In addition to this AFM result, our technique of simultaneous optical detection allows us to distinguish between the two components, unambiguously. The total fluorescence intensity of this system is quite large since there is no electron transfer between the PPV compound and PMMA.

In contrast to the PMMA-containing system, the polymer blends of MDMO-PPV and PCBM (Fig. 2) show much lower absolute fluorescence intensity. This observation confirms that PCBM is a very efficient electron acceptor. Obviously, the quantum efficiency of the radiation-less intermolecular electron transfer from MDMO-PPV to PCBM exceeds the fluorescence quantum efficiency of MDMO-PPV, significantly. The comparison of the topography (Fig. 2a) and the fluorescence intensity (Fig. 2b) shows that a film obtained by spin-coating from a toluene solution contains islands of MDMO-PPV which are embedded in PCBM.

The lateral structure can be clearly seen both in the AFM and in the NSOM images. Moreover, the optical detection enables us to identify which areas correspond to MDMO-PPV and which correspond to PCBM. It is obvious that the hills of the surface correspond to MDMO-PPV whereas the valleys correspond to PCBM. Moreover, the comparison between the NSOM and the AFM images shows that the dark areas in the NSOM image are larger than the respective domains seen in the topography. We attribute this observation to the expected fluorescence quenching appearing in a narrow layer at the MDOM-PPV/PCBM interface. Unfortunately, the difference of the feature sizes at the interface (≈50 nm) is of the same order of magnitude as the size of the aperture of our NSOM probe. Thus, the optical resolution of the NSOM experiment is not sufficient to measure quantitatively the size of the boundary layer in which the fluorescence quenching appears. Nevertheless, the order of magnitude of the deviation between the feature sizes observed in the optical signal and in the topography, respectively, is in agreement with the result of our independent measurement of the thickness of the active layer which is described further.

In this particular system, the pulsed-force mode turned out to be very useful to get a very sharp image of the morphology (Fig. 3). In this mode, the force acting on the AFM cantilever is measured as a function of time while the

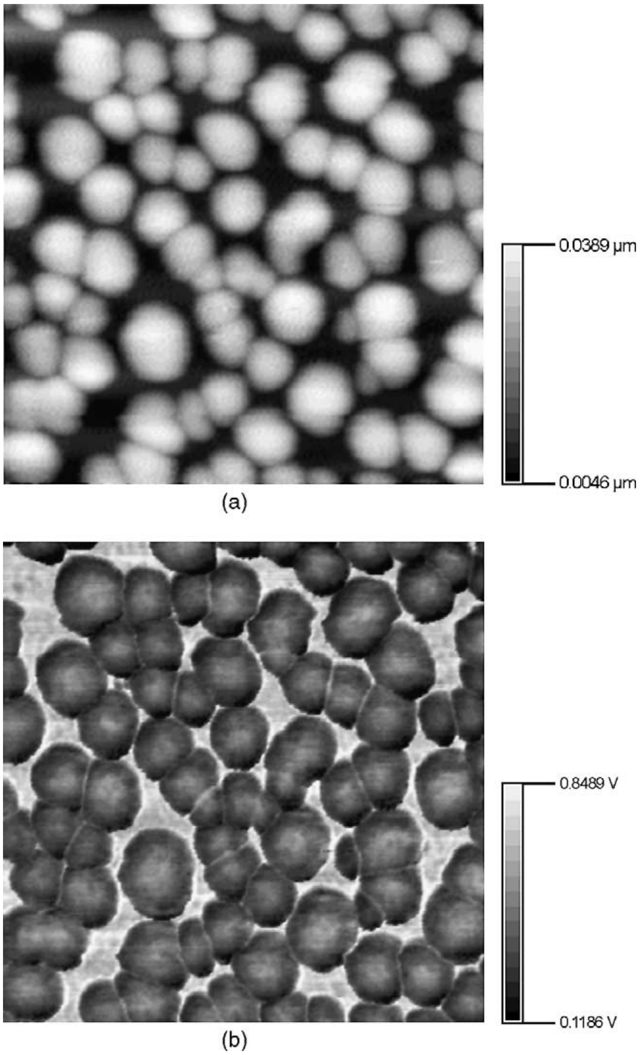


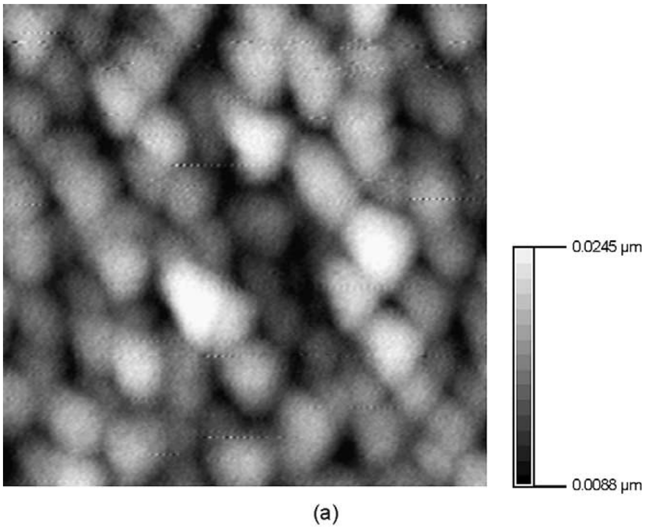
Fig. 3. Topography (a) and pulsed-force AFM ‘adhesion’ signal (b) of a polymer blend consisting of MDMO-PPV and PCBM, as obtained by spin-coating from a solution in toluene. The total area of the image is 2 μm × 2 μm.

cantilever oscillates with a frequency (≈1 kHz) far below the resonance frequency (≈75 kHz) in the vicinity of the surface. The amplitude of the oscillation is large enough so that the tip gets in contact with the sample, periodically. The response depends on mechanical properties of the sample, like stiffness and adhesion. Not surprisingly, the mechanical properties of the conjugated polymer are quite different from those of the fullerene derivative. Thus, this technique results in images with very high contrast (Fig. 3b). The comparison of the pulsed-force AFM image (Fig. 3b) with the optical image (Fig. 2b) shows that the PCBM regions exhibit larger interactions with the cantilever tip. The precise origin of this different interaction is not clear; it might be attributed to the crystalline structure of PCBM or due to different surface conditions.

The topography (Fig. 3a) shows variations in height up to 30 nm which is larger than the height differences (≈8 nm) seen in the sample represented in Fig. 2. Both the order of magnitude of the height variations and the observation of different amplitudes of this variation are in agreement with similar observations by Sariciftci and co-workers [10,16].

In comparison to the blends obtained by spin-coating from toluene solutions, the samples obtained from chlorobenzene show slightly smaller feature sizes and distinctly less sharp phase boundaries (Fig. 4). Both the topography (Fig. 4a) and the pulsed-force ‘adhesion’ signal (Fig. 4b) show a rather smooth variation on the sample surface. This observation confirms earlier studies [10] which have shown that the morphology of the blends has considerable influence on the power conversion efficiency of photovoltaic cells. The less distinct phase boundaries seem to indicate inhomogenities or concentration gradients close to the interface between the two components. Moreover, we cannot exclude that the blend obtained from chlorobenzene forms a bicontinuous network rather than isolated PCBM islands.

In order to investigate the influence of the size of the MDOM-PPV and fullerene (C_{60}) regions on the fluorescence quenching quantitatively, we studied also uniform films of these components with varying film thickness. For this purpose, a glass substrate was covered with a thin layer of MDMO-PPV by spin-coating, and a layer of C_{60} was deposited on a part of the polymer surface by thermal evaporation in high vacuum. The layer thicknesses were varied between 6 and 65 nm. The fluorescence intensity of the two-layer structure was measured in the confocal microscope and compared to the fluorescence intensity of the uncoated polymer film. The results of this relative fluorescence intensity are displayed in (Fig. 5). At constant thickness of the polymer layer, the influence of the thickness of the fullerene layer on the fluorescence is negligible. However, variation of the thickness of the polymer layer at constant thickness



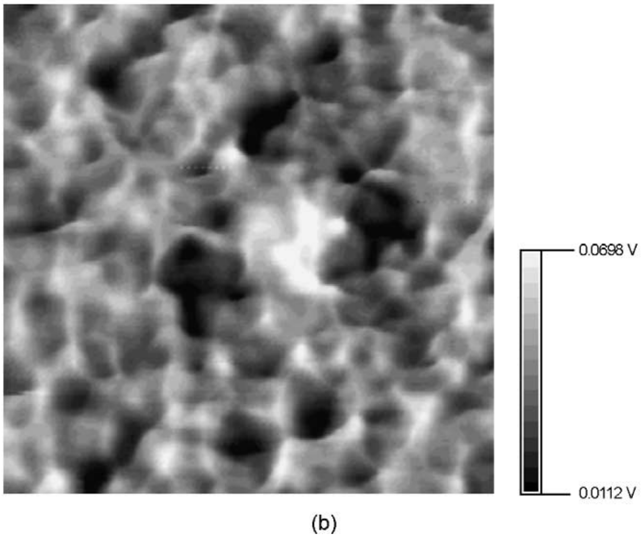


Fig. 4. Topography and pulsed-force AFM ‘adhesion’ signal measured for a polymer blend consisting of MDMO-PPV and PCBM, as obtained by spin-coating from a solution in chlorobenzene. The total area of the image is 2 µm × 2 µm.

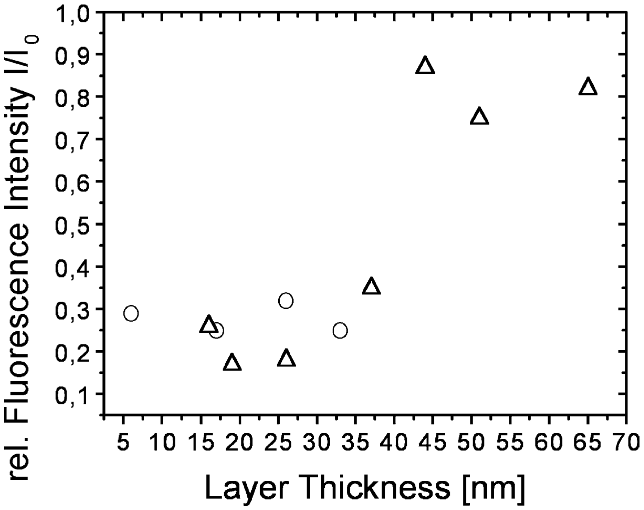


Fig. 5. Relative fluorescence intensity of two adjacent layers, consisting of MDMO-PPV and C_{60}, respectively. (○) Varying layer thickness of fullerene (C_{60}) at constant thickness (≈30 nm) of MDMO-PPV. (△) Varying layer thickness of MDMO-PPV at constant thickness (≈10 nm) of C_{60}.

of the fullerene derivative shows an increase of the fluorescence intensity above a critical layer thickness of 40 nm. This result confirms that the fluorescence quenching is due to the transfer of excited electrons from the conjugated polymer to the fullerene which occurs only within a thin interface layer. The thickness of the latter depends on the exciton diffusion length [17]. Indeed, the critical layer thickness of MDMO-PPV found in our experiment is similar to the exciton diffusion length measured by other techniques [17].

4. Conclusion

Summarizing, the application of both atomic force microscopy and optical near-field microscopy in order investigate the morphology of heterogeneous blends of the conjugated polymer MDMO-PPV and the fullerene derivative PCBM turned out to be very useful. Although the spatial resolution of the optical near-field investigation is rather poor, the excitation at 488 nm enables us to distinguish clearly between the fluorescent polymer and the C_{60} derivative which shows no fluorescence under this condition. By comparison of the NSOM and the AFM images, we can then identify each of the two compounds unambiguously. In particular, the distinct difference of the mechanical properties of the two compounds results in very sharp images when the pulsed-force mode of the AFM is used. In the blends obtained by spin-coating from a solution with toluene, the results indicate that the PCBM regions are connected whereas the MDMO-PPV regions form separated islands. This result may explain the poor power conversion efficiency in this case. In agreement with Shaheen et al. [10], we found smaller feature sizes and an entangled network morphology when the same components are spin-coated from a solution in chlorobenzene. The variation of the film thickness in two-layer samples shows that effective fluorescence quenching in the PPV appears only if the thickness of the PPV layer is below 40 nm. This observation is in qualitative agreement with our NSOM observations and with measurements of the exciton diffusion length in similar systems.

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