Macromol. Symp. **2006**, 233, 203–209 DOI: 10.1002/masy.200650126

Influence of the Nanoscale Morphology on the Photovoltaic Properties of Fullerene/MEH-PPV Composites

Joël Davenas,[1] Pierre Alcouffe,[1] Adnen Ltaief,[1,2] Abdelaziz Bouazizi[2]*

Summary: The relation between morphology and photoelectric properties of PPV derivatives/fullerene composites forming bulk heterojunction solar cells has been investigated. The solvent used to spin cast the photoactive layers has a main influence on the quenching of the MEH-PPV fluorescence, which could be attributed to different dispersion abilities of C_{60} in the polymer layer shown by AFM microscopy. Formation of large fullerene aggregates is observed at fullerene concentrations of the order of 10% leading to phase separation for composite layers processed in THF, whereas more dispersed distributions of fullerenes are observed in an aromatic solvent like ODCB which accounts for a more efficient luminescence quenching with increasing filler concentrations. However the improvement of the dissociation of photogenerated charge pairs is counterbalanced by a less efficient charge transport in the composite shown by lower short circuit currents probably due to unfavorable polymer chain arrangement in ODCB. Thin film processing conditions have been modified by the preparation of blends of solutions of the polymer in THF and fullerene in ODCB. The resulting spin casted layers show improved morphologies implying better dispersion of the fullerenes and increased short circuit currents. The improvement of the photovoltaic properties of the MEH-PPV/C_{60} composites has been attributed to the nanosized fullerene domains formed upon phase separation.

Keywords: atomic force microscopy (AFM); conjugated polymers; luminescence; photovoltaic; spin coating

Introduction

Polymer based devices for the conversion of solar energy into electrical power have led to an expanding interest due to the fantastic reduction of the cost expected from the production of large area solar cells by printing techniques. Such molecular solar cells however exhibit presently too low photovoltaic (PV) conversion efficiencies to ensure viable energy production. Progress needs decisive improvement of the control of the PPV derivative/C_{60} composites to form dispersed heterojunction systems allowing simultaneously efficient separation of the photogenerated charge pairs and their transport to the opposite electrodes to be collected.[1] The ideal system would need the dispersion of C_{60} at the molecular level to achieve efficient charge separation, whereas fullerene concentrations above the critical concentration are needed to produce percolation paths for electron collection. In fact the formation of fullerene aggregates cannot be avoided due to the difficulty of achieving good dispersions of C_{60} at concentrations higher than 10%. A good compromise between the efficiencies of charge separation and transport through the photoactive layer can be obtained for

---

[1] Ingénierie des Matériaux Polymères, CNRS - Université Claude Bernard-Lyon 1, 43 Bd du 11 Novembre, 69100 Villeurbanne, France
E-mail: Joel.Davenas@univ-lyon1.fr
[2] Laboratoire de Physique et Chimie des Interfaces, Faculté des Sciences de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisie

domain sizes of the same order than the diffusion length of the exciton formed by the electron hole pairs generated under sun exposition. The purpose of this paper was to investigate the influence of the morphology on the photoelectric properties of MEH-PPV/C_{60} composites. The role of the solvent and of the fullerene concentrations will be emphasized.

Experimental

Materials supplied by sigma Aldrich were poly[2-methoxy, 5-(2′-ethylhexyloxy)-1,4,-phenylene-vinylene] (MEH-PPV) for the hole transporting layer and fullerenes (C_{60}) as electron acceptors. MEH-PPV has a molar mass of 86 000 g/mol determined by gel permeation chromatography (GPC). MEH-PPV and C_{60} were dissolved in tetrahydrofuran (THF) or orthodichlorobenzene (ODCB) at a concentration of 15 mg/ml and the solutions were stirred for several hours. 1, 3, 6, 9, 10, 20, 30 and 40% C_{60}/MEH-PPV + C_{60} blend compositions were obtained by mixing the respective solutions. Each component was dissolved in its appropriate solvent (MEH-PPV in THF, C_{60} in ODCB) in the modified procedure. Suprasil substrates were used for UV-visible spectrophotometry and photo-luminescence spectroscopy. Glass coated with indium-tin-oxide (ITO) were used as substrates in the photovoltaic structures (anode of the diodes). The ITO substrates were cleaned in an ultrasonic bath of acetone (HPLC grade) for 20 mn, followed by isopropyl alcohol (IPA) (HPLC grade) rinsing for 20 mn at room temperature, before being dried in a nitrogen gas flow. Photoactive layers were produced by spin coating (2000 rpm for 20 s) the MEH-PPV/C_{60} solution onto ITO substrates using a "P6700 Series" spin coater. Top contacts (cathode of the diodes) were deposited through a shadow mask by evaporation in vacuum at a pressure below 10^{-5} Torr. The thickness of the polymer/fullerene layers was of the order of 500 nm and the device area 10 mm^2. UV-VIS spectra were performed over the 190–900 nm spectral range using an "UVIKON 941 plus" spectrophotometer. Photoluminescence spectra were recorded using a "Jobin Yvon-SPEX Spectrum One" CCD detector, cooled at liquid nitrogen temperature. The short circuit current and I-V curves were measured using a "Keithley 236" source unit, under illumination with an Halogen lamp. AFM imaging was performed using a "Nanoscope IIIa Digital Instruments" microscope. All processing steps were carried out in clean room conditions and the measurements were performed in air.

Results and Discussion

Influence of the Solvent on the Morphology

The UV-visible absorption spectra and photoluminescence (PL) response of MEH-PPV thin films performed from THF or ODCB solutions shows small solvent dependence of the UV-visible absorption spectra (Figure 1a) whereas the PL spectra (Figure 1b) exhibit a clear effect of the solvent.

In fact, the slight shift of the absorption edge near 580 nm corresponds to a small variation of the optical band gap which is representative of the bulk properties. The photoluminescence spectrum is more dependent on the chain conformation since resulting from the recombination of excitons, which may be formed by charges on the same chain or on distinct chains in interaction. The emission component at 630 nm is more intense for THF films than for the ODCB processed one. This red shifted component is due to excimer emission indicative of strong interactions between neighboring polymer chains.[2]

The AFM topography of (10 wt. %) MEH-PPV/C_{60} films processed from THF shows (Figure 2) large islands at the surface of the THF coated film, which result from the formation of fullerene clusters. In contrast, the surface of the spin casted film from ODCB appears much more uniform due to a better fullerene dispersion.

However AFM provides a top view of the surface which tend to flatten its real roughness. To get a more precise view of the surface according to the solvent used to produce the film, scanning electron microscopy (SEM) has been used to image the cross sections of samples after having broken them.

Whatever the solvent used, very uneven surfaces are observed (Figure 3) for the fullerene concentration (40 weight %) which must be reached to induce the formation of a continuous path for electronic conduction through the composite layer.[3] The emergence of fullerene islands at the surface shows that demixion effects appear at high concentration leading to a very inhomogeneous photoactive layer. A loss of efficiency is expected from the fullerene molecules which are no more in intimate contact with the polymer. The most common way to improve the miscibility of both components is to use PCBM: 1-(3-methoxycarbonyl) propyl-1-phenyl-[6,6]C_{61}, a derivative of C_{60} which is functionalised by a side chain.[4,5] However large aggregation effects leading to the formation of pure PCBM domains is still observed in this case.[6] We have investigated another processing route based on the production of blends of solutions of each component in its good solvent (MEH-

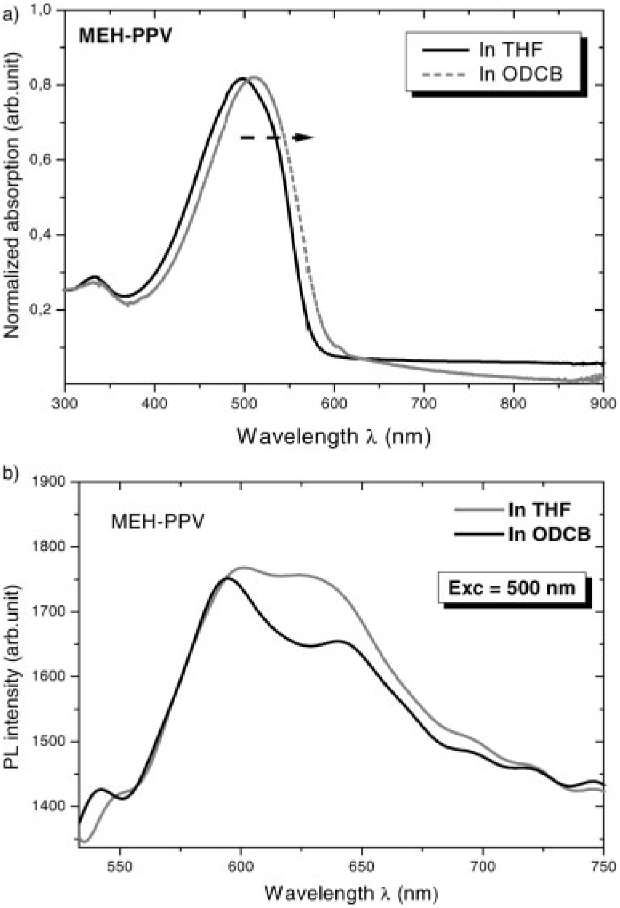


Figure 1.
(a) Optical absorption spectra of MEH-PPV thin films from THF or ODCB solutions. (b) Photoluminescence spectra of MEH-PPV thin films casted from THF or ODCB.

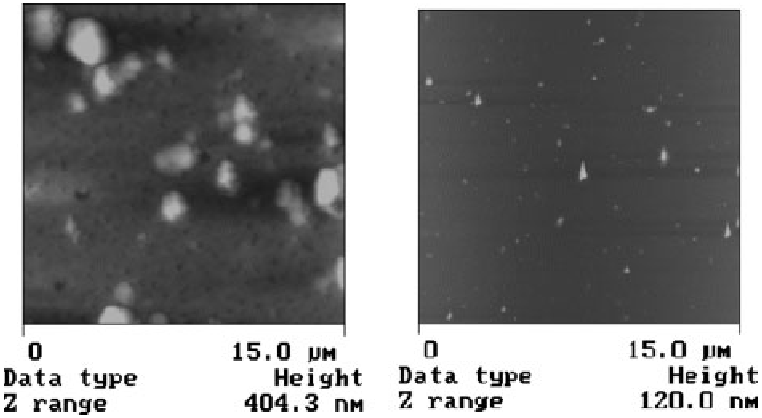


Figure 2.
AFM topography of MEH-PPV/C_{60} composites casted from THF or ODCB.

PPV in THF, C_{60} in ODCB) in the appropriate proportions. Spin casting of the blend solution leads to the formation of much more homogeneous layers indicated by SEM imaging of the surfaces (Figure 4) and improved dispersion of fullerenes. AFM characterization shows that fullerene clusters of about 100 nm diameter are then homogeneously distributed all over the film (Figure 5).

Blend Composition Effects on the Photoelectric Properties

The influence of the fullerene concentration on the dissociation of the photogenerated charge pairs forming excitons has been studied by the quenching of the photoluminescence for films casted from each solvent (THF, ODCB) and from the blend of solutions. Figure 6 shows a rapid extinction of the luminescence with increasing fullerene concentrations for films processed from ODCB, whereas PL quenching is slower for films casted from THF due to the less efficient charge pair separation since only C_{60} molecules at the surface of aggregates are active, excitons being dissociated before reaching core fullerenes. This finding is confirmed by the incomplete quenching of the luminescence for films

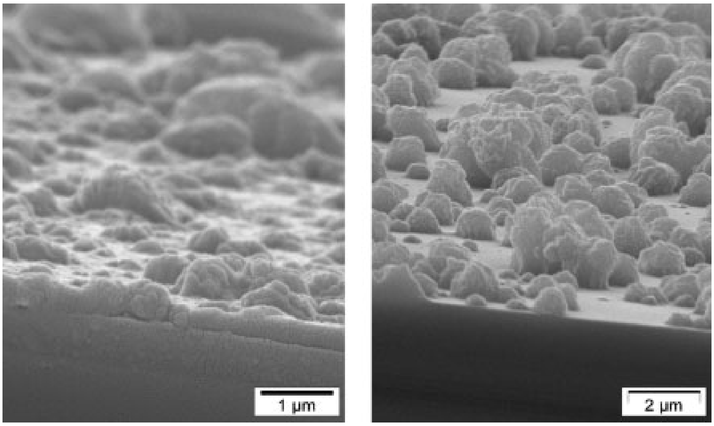


Figure 3.
SEM views under grazing incidence of the surface of MEH-PPV/C_{60} composites (40 weight % C_{60}) processed from THF or ODCB solutions.

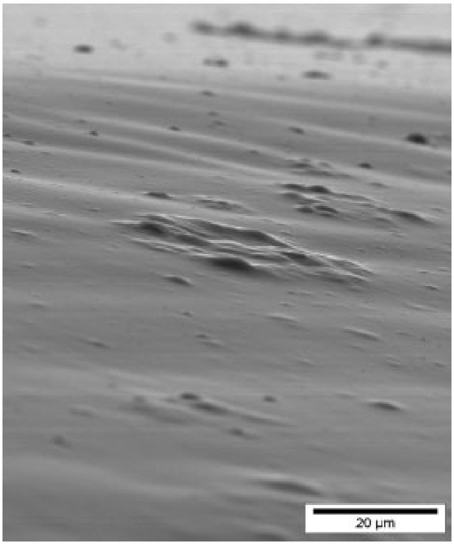


Figure 4.
SEM view of MEH-PPV/C_{60} films cast from (MEH-PPV in THF, C_{60} in ODCB) blends.

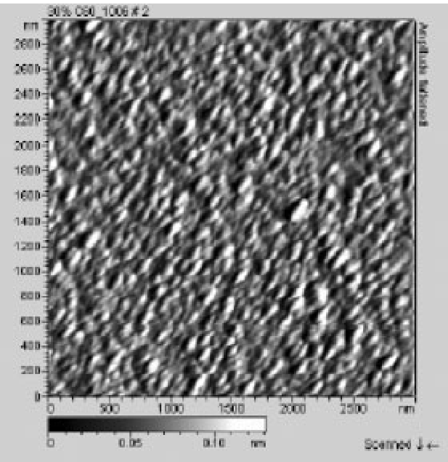


Figure 5.
AFM topography of 25 weight % MEH-PPV/C_{60} films cast from (MEH-PPV in THF, C_{60} in ODCB) blends.

prepared in THF than those in ODCB because of the lower proportion of active molecules for a same total number of $C_{60.}$ A new increase of the photoluminescence is observed above 10% of fullerene in THF casted films. This evolution could mean that the polymer matrix contains increasing volume free from C_{60}, allowing radiative decay due the blend demixion indicated by SEM (Figure 7) leading to phase separation. As was previously expected in the discussion of the surface morphologies, the fullerene structures emerging from the surface also contribute to the reduction of PL quenching efficiency.

Films casted from the blend of solutions shows the faster quenching of the polymer luminescence, indicating a more efficient dissociation of the photogenerated charge pairs, without the PL recovery observed for

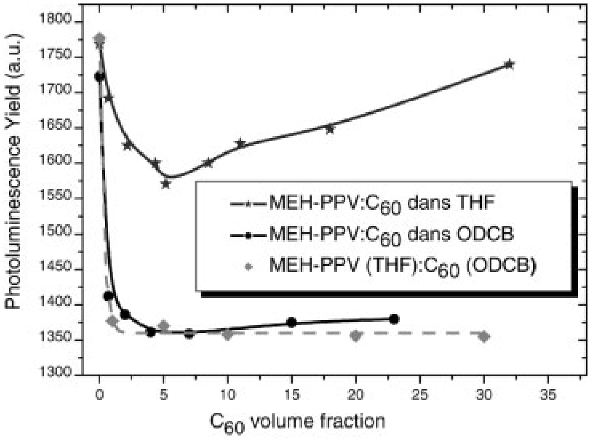
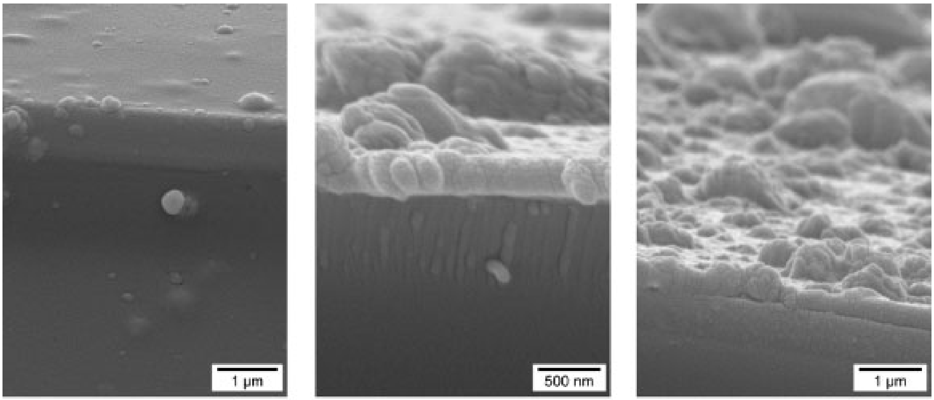


Figure 6.
Quenching of the photoluminescence with increasing fullerene concentration for the different morphologies.



0 % 20 % 40 %

Figure 7.
SEM views of the surface MEH-PPV/C_{60} composites casted from THF, for different fullerene concentrations.

films processed in THF and in a lower extent ODCB.

It is then possible to conclude that the size of the polymer domains left by the uniform filling of the thin films by fullerene clusters is smaller tham the exciton length, which is of the order of 10 nm. The following step is then to consider how this nanoscale morphology influences the transport of the dissociated charges.

We have studied the final effect of the blend composition on the photoelectric properties shown by the current-voltage characteristics under illumination in Fig. 8.

Films processed from THF solutions give rise to a larger short circuit current than ODCB in spite of a better efficiency for charge pair dissociation in the last case. It appears that the closer chain packing, indicated in Figure 2 by the excimer

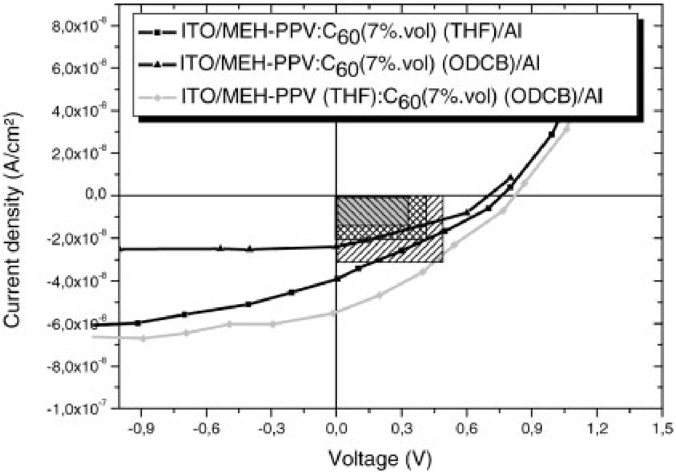


Figure 8.
Photoelectric response of MEH-PPV/C_{60} composites for the different solvents.

component of the luminescence rsponse, leads to higher photocurrents due to easier interchain charge hopping. However a larger shunt resistance, indicated by the slope of the tangent at short circuit ($V = 0$), shows that the current is space charge limited due to high trap concentrations.[7] This behaviour shows that fullerene dispersion and polymer chain conformations both influence the final photovoltaic response. At last the films processed from the blend of solutions of each component exhibits the best photovoltaic properties characterized by the highest short circuit current and open circuit voltage. The nanoscale morphology of the films resulting from this new processing procedure leads simultaneously to charge separation and transport improvement.

Conclusions

The morphology has a dramatic influence on the photovoltaic properties of MEH-PPV/C_{60} composites both at the molecular level (polymer chain packing) and at the nanoscale (phase separation). A new route based on the dissolution of the polymer and fullerenes in their good solvent and casting of the blend of these solutions led to the formation of composites exhibiting a more homogeneous dispersion of nanosized C_{60} clusters. These nanocomposites simultaneously show an increase of the dissociation efficiency and transport of the photogenerated charges leading to photovoltaic properties improvement. In conclusion progress is possible through an improved control of the processing conditions of the nanocomposite. This work is presently extended to the control of the interfaces between the photoactive composite and electrode materials to optimize these photovoltaic cells.

Acknowledgements: Support by Ministry of Foreign Affairs through the cooperation programme CMCU with Tunisia (project ''Role of the interfaces in molecular electroluminescent and photovoltaic devices'') is acknowledged.

[1] J. Nelson, Materials Today **2002**, *5*, 20
[2] Y. Shi, J. Liu, Y. Yang, J. Appl. Phys. **2000**, *87*, 4254
[3] A. ltaief, A. Bouazizi, J. Davenas, R. Ben Chaabane, H. Ben Ouada, Synth. Met. **2004**, *147*, 261
[4] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, Adv. Fonct. Mat. **2001**, *11*, 15
[5] H. Kim, J.Y. Kim, K. Lee.Y. Park, Y. Jin, H. Suh, Curr. Appl. Phys. **2001**, *1*, 139
[6] H. Hoppe, M. Niggeman, C. Winder, J. Kraut, R. Hiesgen, A. Hinsch, D. Meissner, N.S. Sariftci, Adv. Funct. Mat. **2004**, *14*, 2004
[7] J.M. Nunzi, C.R. Phys. **2002**, *3*, 523
[8] R. Pacios, D.D.C. Bradley, Synth. Met. **2001**, *9149*, 1