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Polymers for opto-electronic applications: structure and morphology of thin films and their interfaces

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Abstract

Organic–organic and metal–organic interfaces are explored. The influence of the morphology of thin films of MEH-phenylene-vinylene oligomer (OPV5):C₆₀ blends on their photovoltaic characteristics is demonstrated. An interdigitating structure is considered to be favorable for efficient operation. The design of a diblock copolymer for this specific application is discussed. By means of UPS, the electronic energy levels at the interface between OPV5 and gold are assessed. Due to the formation of a dipole layer, the vacuum levels are not aligned and the barrier for charge injection is altered. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Interfaces; Morphology; Block copolymers; Photovoltaic cells; Ultraviolet photoelectron spectroscopy

1. Introduction

Organic opto-electronic devices are multi-component systems by their nature, comprising one or more organic layers and the electrodes. Inevitably, interfaces between these very different components must play a crucial role to the performance of the devices. Since charge transport occurs via these interfaces, one should be concerned with their character in many respects, and at length scales ranging from the molecular to the macroscopic.

In this paper it is demonstrated how electronic processes occurring at organic–organic interfaces may benefit from a particular interface morphology. This is explored for the case of photovoltaic devices. The design of a block copolymer for this specific application is discussed. Finally, electronic effects associated with the deposition of an organic molecule on a metal will be described. This process involves shifts of the electronic levels and affects charge injection.

2. Results and discussion

2.1. Interface morphology in photovoltaic devices

In organic semiconductors, light absorption creates bound electron–hole pairs (excitons). In photovoltaic composites of

the donor–acceptor type [1], the dissociation of the exciton into charge carriers is accomplished by a charge transfer from donor to acceptor, occurring at their interface. After transfer, separation and transport of the opposite charges takes place under the influence of the built-in electric field caused by the asymmetric contacts. The performance of this type of device is very sensitive to the morphology of the blend. Since the exciton diffusion range is typically shorter than the light absorption depth, a properly dimensioned network of donor–acceptor heterojunctions [2,3] should be more efficient in terms of the exciton dissociation than a planar double-layer structure. However, a network system may have features that degrade performance, such as phase discontinuities and increased molecular mixing. These may cause energy level disorder, create charge traps and, hence reduce the carrier mobility. This section reports on a comparative study of blends and double-layers of MEH-phenylene-vinylene oligomer (OPV5):C₆₀ (Fig. 1) concerning morphologies and photovoltaic characteristics [4]. The efficient quenching of photoluminescence (from MEH-OPV5) in such blends indicates photoinduced charge transfer to C₆₀ acting as the electron acceptor (Fig. 1). In the photovoltaic device, the organic layer was prepared by vacuum deposition in two different ways: (i) codeposition, i.e. MEH-OPV5 and C₆₀ are deposited simultaneously on an ITO substrate, and (ii) consecutive deposition, i.e. the deposition of MEH-OPV5 on an ITO substrate is followed by deposition of C₆₀.

The relatively high value of the dark current for the codeposited device in reverse bias is an indication of a continuous phase of C₆₀ between the electrodes (Fig. 2A).

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Fig. 1. Photoluminescence quenching in MEH-OPV5:C₆₀ composites: (A) blend film obtained by codeposition; (B) double-layer film.

Fig. 2. (A) Device characteristics of ITO/codeposited MEH-OPV5:C₆₀/Al and (B) ITO/consecutively deposited MEH-OPV5:C₆₀/Al. (i) *I*–*V* curves in the dark (solid circles) and under illumination ($\lambda = 458$ nm, 1 mW/cm²; open circles). (ii) Dependence of photosensitivity and open-circuit voltage on incident light intensity.

The strong increase of the dark current in forward bias above 0.5 V reflects a current through the MEH-OPV5 phase. Hence, the blend is indeed co-continuous. The open-circuit voltage saturates at about 0.5 V, corresponding to the difference of the work functions of Al and ITO. Unlike the codeposited device, the consecutively evaporated one shows almost symmetrical *I*–*V* characteristics in the dark (Fig. 2B). Surprisingly, the photovoltaic characteristics of the consecutively deposited device at zero bias are quite similar to those of the codeposited one. The photosensitivity is about 100 mA/W, the monochromatic power conversion efficiency is around 2%. The unexpected properties of the consecutively deposited device can be explained on the basis of its morphology. According to our AFM studies, the layer of MEH-OPV5, deposited first, forms islands on the substrate. By subsequently depositing C₆₀ until it comprises the entire top surface, a device is created in which C₆₀ makes contact with both electrodes but MEH-OPV5 does not (Fig. 3b). Thus, the interfacial donor–acceptor area is much larger than that of a planar double-layer. This interdigitating

morphology can be regarded as intermediate between a truly planar double-layer film and an interpenetrating blend, but without the limitations to transport of the latter. We expect that an optimized device having this type of morphology will have superior properties.

2.2. Block copolymers for photovoltaics by means of “living” free radical polymerization techniques

Continuous phases, a proper scale of phase separation, and absence of charge traps are major requirements for efficient operation. To achieve control over the phase separation, one may use block copolymer strategies. We synthesized copolymers consisting of a PPV block and a styrene block functionalized with C₆₀. First, a soluble 2,5-dioctyloxy-PPV block (8–10 repeat units) containing one aldehyde group at the chain-end was formed through a Siegrist polycondensation [5]. By condensation with an alkoxyamine-derived Grignard reagent, a macroinitiator for controlled “living” free radical polymerization was obtained.

Fig. 3. Models for the morphology of the active layer in MEH-OPV:C₆₀ devices: (a) codeposited; (b) consecutively deposited.

Fig. 4. UPS spectra and energy diagram for the interface between P5V4 and gold.

Polymerizations with this macroinitiator were carried out in bulk at 125°C, using mixtures of styrene and 4-chloromethylstyrene. The latter allows the incorporation of C₆₀ via atom transfer radical addition. NMR as well as GPC indicated a steady growth of the styrenic block with time (3000–30 000 g/mol). The C₆₀-functionalized block copolymer exhibited strong PL quenching (more than three orders) compared to that of the unfunctionalized polymer. Morphology and photovoltaic properties are currently under study.

2.3. Energy level shifts at the metal–organic interface

For charge transport in devices, the position of the energy levels directly at the metal–organic interface is most relevant [6]. Ultraviolet photoelectron spectroscopy (UPS) measures the energy levels at the interface directly, by probing a layer of organic material deposited onto a metal. Here we report UPS measurements on the interfaces between metals (Au and Ag) and two five-ring oligomers: unsubstituted OPV5 (P5V4; Fig. 4) and MEH-OPV5 (Fig. 1) [7]. In Fig. 4, the interfacial energy diagram is deduced from the HeI UPS spectra of Au (left) and P5V4 on Au (right). The position of the vacuum levels is found by adding 21.2 eV ($h\nu$) to the low-kinetic-energy cut-off values, yielding $E_{\text{vac}}(\text{Au})$ and $E_{\text{vac}}(\text{P5V4})$. Since the cut-off energies differ, the vacuum levels are not aligned, but shifted by $\Delta = E_{\text{k}}^{\text{min}}(\text{P5V4}) - E_{\text{k}}^{\text{min}}(\text{Au})$. This shift reflects the presence of an electric field at the P5V4/Au interface, it points from the oligomer ($\delta+$) to the metal ($\delta-$). The shift directly affects the barrier for hole injection, $\varepsilon_{\text{V}}^{\text{F}}$. It makes hole injection from Au to P5V4 more difficult, but reduces the energy barrier for electron injection into the LUMO of P5V4. The mechanism creating the interface dipole remains to be found; our further results indicate that one or very few molecular layers are involved in the process. Due to the shifts, which are negative in all cases

Table 1
Electronic characteristics of oligomer–metal interfaces^a

Interface	Δ (eV)	I_{s} (eV)	$\varepsilon_{\text{V}}^{\text{F}}$ (eV)	$\varepsilon_{\text{V}}^{\text{F}}$ (eV)
P5V4/Au	-1.0 ± 0.1	5.6 ± 0.1	1.4 ± 0.1	1.5 ± 0.3
P5V4/Ag	-0.4 ± 0.1	5.6 ± 0.1	1.7 ± 0.1	1.6 ± 0.3
MEH-OPV5/Au	-1.2 ± 0.1	5.2 ± 0.1	1.2 ± 0.1	1.3 ± 0.3
MEH-OPV5/Ag	-0.5 ± 0.1	5.3 ± 0.2	1.3 ± 0.2	1.4 ± 0.4

^a Δ : vacuum level shift; I_{s} : ionization energy; $\varepsilon_{\text{V}}^{\text{F}}$: hole injection barrier $E_{\text{F}} - E_{\text{HOMO}}$; $\varepsilon_{\text{V}}^{\text{F}}$: hole injection barrier $I_{\text{s}} - \Phi_{\delta} - \Delta$ ($\Phi_{\text{Au}} = 5.1$ eV, $\Phi_{\text{Ag}} = 4.4$ eV).

investigated, the hole injection barrier is nearly insensitive to the workfunction (Φ) of the metal or the ionization potential (I_{s}) of the oligomer (Table 1). Knowledge of the interfacial dipole layer is therefore crucial for understanding the electrical characteristics of organic-based electronic devices and for improving their design.

3. Conclusion

In the context of opto-electronic devices, important aspects of interfaces have been demonstrated: (i) the role of interface morphology to the efficiency of device operation; (ii) the design of block copolymers for controlled phase separation; (iii) the presence of a dipole at the metal–organic interface, affecting the relative position of electronic energy levels.

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