

Spectroscopic investigation of the interfaces in new poly(9,9-dihexyl-9H-fluorene-2,7-diyl) based electroluminescent devices

C. Donitsi^{1,*}, I. Alexandrescu¹ and M. Aleksandrova²

¹University of Craiova, Department of Applied Chemistry, Craiova, Str. Calea Bucuresti, 7. Bulgaria

²Technical University of Sofia, Department of Microelectronics, Sofia, Kl. Ohridski, 8. Bulgaria

Received 10 March 2010; Revised 31 October 2010; Accepted 25 January 2011

Abstract

The highest occupied and lowest unoccupied states of the new electroluminescent material poly(9,9-dihexyl-9H-fluorene-2,7-diyl) (PPV-D) and polyvinylcarbazole (PVK) are investigated using ultraviolet photoelectron and inverse photoemission spectroscopies. Hole injection barriers are determined for interfaces between indium-tin oxide covered substrates with work function ranging from 4.4 to 4.7 eV and these two polymers. Vacuum level alignment with flat bands away from the interface is found when the interface hole barrier is 0.6 eV or larger. Band bending away from the Fermi level occurs when the hole barrier is smaller than 0.6 eV. This is due to the accumulation charges at the interface with the polymer when the injection barrier is small. The resulting field bends the polymer levels to limit charge incoming in the bulk of the film. The efficiency of the electroluminescent structures is strongly influenced by the different energy levels alignment at the layer interfaces.

Keywords: polymer electroluminescent devices, energy level measurement, interface optimization.

1. Introduction

The parameters and characteristics of polymer light-emitting devices (PLED) are considerably improved since the first demonstration of practical devices based on poly(p-phenylene vinylene) (PPV) [1]. The ease of processing in form of thin films by spray deposition [2], spin- and dip-coating [3], etc. is key advantage of the polymeric materials for cheap large-scale production. Yet, some fundamental properties of these materials and their interfaces in devices are difficult to be determined and are still under intensive investigation. From practical importance for the PLED efficiency are charge injection and transport through the thin films in the structures [4]. Energy level alignment across the electrode/polymer interfaces is crucial for the device performance. The main idea is to obtain small enough contact barriers for Ohmic hole and electron injection in the electroluminescent layer [5].

The determination of the interface energetic is more difficult for structures with polymer films than for small organic molecular films because of the materials nature, which consist of long chains along which the charge carriers can be delocalized and present complex interchain interactions. The film morphology, which is difficult to control, greatly affects the electronic and optical properties of these materials [6]. The morphology of the polymer films is therefore a source of additionally difficulties in the interpretation of information, obtained from spectroscopic techniques used in the investigation of interfaces. Ultraviolet

photoelectron and inverse photoemission spectroscopies provide the most direct way for experimentally estimation of occupied and unoccupied electronic states in the bulk and at interfaces.

In this work, multilayer polymeric structure based on poly(9,9-dihexyl-9H-fluorene-2,7-diyl) (PPV-D) new and still weakly investigated electroluminescent material is chosen. Polyvinylcarbazole (PVK) is used as hole transporting layer. PVK has been extensively studied as hole transporting layer in Alq₃ based devices [7,8], but not enough in multilayer polymer based structures. For PPV-D still there is no information about measurements of its energy levels position and energy level offset at the electrode interfaces. We investigate these materials with ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES).

2. Experimental Section

In these experiments a highly pure form of commercially available PPV-D and PVK polymers (Sigma-Aldrich) was used for fabrication of the thin films. The chemical structures of the used polymers are shown on Fig. 1. For the PPV-D film preparation with thicknesses from 30 to 200 Å, solutions containing 0.2-1.8 mg granules dissolved in 25 mL of chloroform were spray deposited. The substrate temperature was set to 60°C. PVK films are deposited at the similar conditions. The used spray deposition setup, as well the optimized conditions for obtaining of uniform polymer

layers by pulverization are described in detail in [9]. The substrates were ITO covered glasses. ITO playing role of anode was obtained by RF reactive sputtering. Onto the ITO electrode were deposited PVK and PPV-D. All films thicknesses were measured by Atom Force Microscope (AFM).

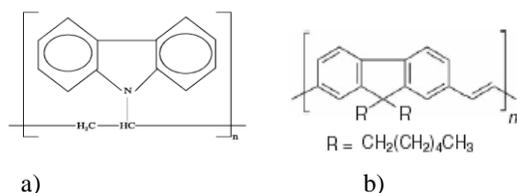


Fig. 1. Chemical structure of the used polymers: a) PVK and b) PPV-D.

Measurements of occupied and unoccupied electronic states of the polymer films were performed with UPS and IPES, respectively. UPS was carried out with the He I (21.22 eV) and He II (40.8 eV) photon lines from a He-discharge lamp and a double-pass cylindrical mirror analyzer for electron collection. IPES was carried out with an electron current density of $\sim 0.8 \mu\text{A}/\text{cm}^2$ impinging on the surface. The ionization potential (IP) of each film (200 Å) was determined as energy difference between the vacuum level (E_{vac}) and the edge of the highest occupied molecular orbital (HOMO), following a procedure described elsewhere [10]. By analogy the electron affinity (EA) for each film was determined as the energy difference between E_{vac} and the edge of the lowest unoccupied molecular orbital (LUMO). Polymer films were additionally made thinner to about 30 Å for the measurements with UPS and IPES to ensure that no charging occurred in either experiment.

3. Results and Discussion

The combined UPS and IPES spectra from 200 Å thick PVK and PPV-D films on ITO are shown in Fig. 2a and 2b. The work function of the ITO substrates measured on a control sample prepared at the same time and under the same conditions as the substrates used for the polymer films, is 4.71 ± 0.05 eV. The IPs of PVK and PPV-D are 5.04 ± 0.05 eV and 5.23 ± 0.05 eV, and the corresponding EAs are 2.55 ± 0.08 eV and 2.45 ± 0.08 eV, respectively. The edge-to-edge gap, measured between the onsets of occupied and unoccupied states (IP - EA), is 2.49 for PVK and 2.78 for PPV-D.

Values for PVK HOMO and LUMO positions of 5.02 and 2.09 eV are reported [12]. Therefore the spectroscopic measurements are in good agreement with the achieved in the literature. This allows a precise determination not only of the relative positions of HOMO and LUMO levels, but of the energy gap between them. The differences in the values might be due to the different environments in which the measurements are made. The energy gap known as transport gap E_t represents the energy difference between a “free” electron (or negative polaron) and a “free” hole (or positive polaron), separated in space and moving through the polymer. With some corrections related to surface vs. bulk polarization and relaxation processes in the chain the separation between the LUMO and HOMO determined by IPES and UPS is precisely this transport gap. This gap is fundamentally different from the optical absorption gap, E_{opt} , which represents the energy necessary to excite an electron

on a polymer chain and create a bound electron-hole pair, i.e., an exciton. The energy difference between E_t and E_{opt} represents the energy necessary to break the exciton to create a free electron (or negative polaron) and a free hole (or positive polaron), i.e., the exciton binding energy E_B . Using the procedure developed for molecular films [13] we found that E_t is equal to 2.49 eV for PVK and 2.78 eV for PPV-D. From measured E_{opt} of ~ 2.8 eV and ~ 2.1 eV for both materials, the estimated E_B is 0.14 and 0.15 eV for PVK and PPV-D, respectively. These values give an idea that exciton binding energies in these polymer films are significantly low (an order of magnitude lower) than in some small molecular compound [14]. This is a proof that the investigated combination of polymers is suitable not only for light-emitting application, but for polymer solar cells, where the binding energy must be low enough for fluently extraction of the charge carriers through the electrodes.

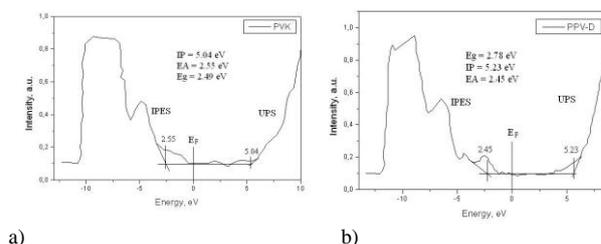


Fig. 2. Combined UPS/IPES spectra of 200 Å thick films of: a) PVK and b) PPV-D sprayed on ITO. The Fermi level (E_F) is the reference energy.

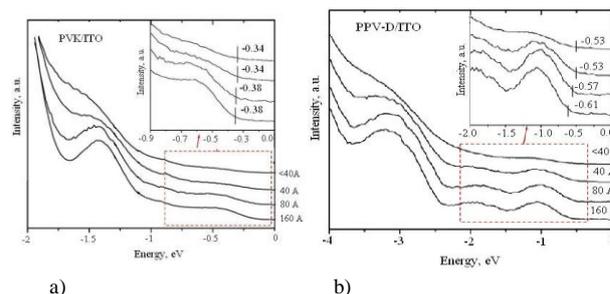
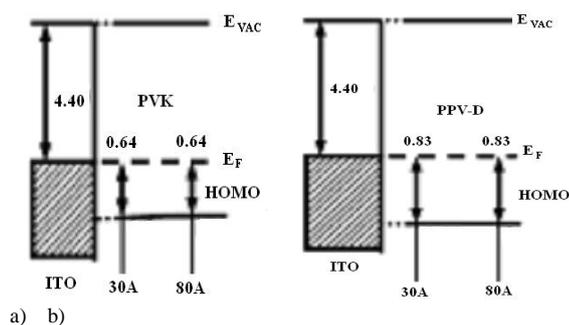


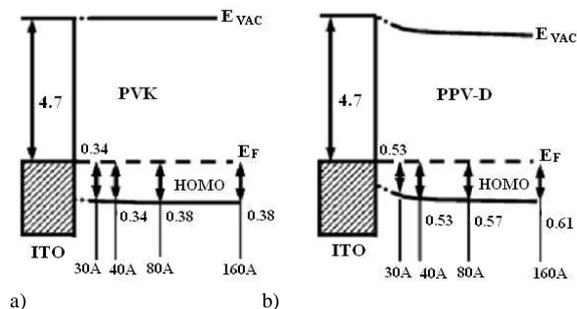
Fig. 3. UPS spectra of films with varying thickness sprayed on ITO: a) PVK and b) PPV-D. Enlarged views of the hole injection barriers are shown in the inset.

For PVK, the assumption of flat bands holds, as the hole injection barrier (measured at the surface of the film) is nearly identical (0.34-0.38 eV) to the difference between the IP of the polymer (5.04 eV) and the work function of the ITO substrate (4.7 eV), which indicates an interface electronic structure defined by vacuum level alignment between the polymer film and substrate. On the other hand, the energetics of the ITO/PPV-D interface is different. If vacuum level alignment did occur at the interface, the hole injection barrier would be exactly the difference between the IP of both polymers, which is about 0.5 eV. But hole barrier of 0.61 eV is measured at the free surface of the PPV-D film, which leads to a value of the work function of the film (i.e., $E_{\text{vac}} - E_F$) ~ 0.11 eV smaller. The difference must therefore be attributed to the formation of an interface dipole and band bending at the polymer interface, or both. This can be due to the fact that polymer films are deposited from solution in ambient environment on a substrate surface, during which they are contaminated with hydrocarbons and/or oxides. No additional interface-related features are

detected via UPS on films with decreasing thickness, suggesting minimal chemical interactions between the polymers and the ITO substrate (Fig. 3). A negligible shift of the HOMO level toward the Fermi level is observed for PVK with decreasing thickness, but the shift is consistently larger than 0.1 eV in the case of PPV-D. According to the experiments described above, when the polymer film is deposited on a (relatively) low work function substrate, leading to a hole barrier larger than 0.6 eV, the energy of the polymer levels remains constant (flat) across the film, from interface to free surface (Fig. 4). On the other hand, when the polymer film is sprayed on a high work function substrate, leading to a smaller hole barrier of the order of 0.3-0.5 eV, the molecular levels are seen to bend away from their interfacial position (Fig. 5).



a) b)
Fig. 4. Energy diagrams of a) PVK/ITO; b) PPV-D/ITO, when the work function of ITO is relatively low.



a) b)
Fig. 5. Energy diagrams of: a) PVK/ITO; b) PPV-D/ITO, when the work function of ITO is relatively high.

This result is to be compared with the results obtained by Tengstedt et al. [15] on various polymers, including F8 (PFO) and TFB who report Fermi level pinning and an interface hole barrier of ~ 0.6 eV when the polymer film is spun on a high work function substrate. A probable explanation for this type of behaviour is an excess density of charges accumulates in the organic material (holes in the present case). These interface charges induce an electric field that displaces the frontier orbital, e.g., the HOMO level, away from E_F , limiting further penetration of charges into the bulk of the film, via a kind of self-regulating

mechanism. The density of excess interface charges depends on the barrier. When the barrier is < 0.6 eV, the density of excess holes is sufficient to bend the bands within the thickness measured by UPS (< 200 Å). On the other hand, when the hole barrier is > 0.6 eV, the charge density is small and the field does not induce a significant band bending over the range of thickness investigated here. This behaviour is closely related with the device efficiency. Fig. 6 illustrates the quantum efficiency QE as function of the applied voltage for the above described cases. If PVK film is inserted in structure ITO/PPV-D/Al, it will transport effectively the holes injected from the ITO anode to PPV-D, because the injection barrier at the anode is reduced from 0.83 eV to 0.64 eV. Most of the anode barrier remains at the ITO/PVK interface, which is however more conducting, whereas the barrier at the PVK/PPV-D interface is lower. This balance is favorable for the injection efficiency and therefore for the luminous efficiency.

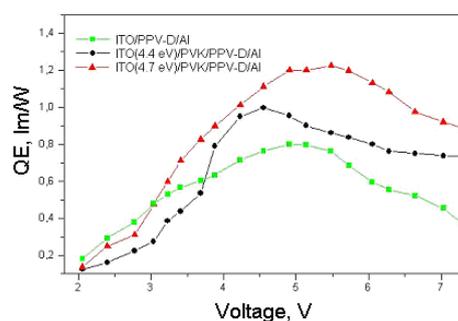


Fig. 6. Quantum efficiency of PPV-D based electroluminescent structure as function of the applied voltage, according to the energy level alignment at the anode interface.

4. Conclusion

The UPS and IPES investigations of important for organic light-emitting application polymers, such as PVK and PPV-D provides an accurate determination of the energy position of the transport states, and thus a solid basis for further study of the electronic structure of the polymer-metal interfaces in such devices. The energetics of interfaces between PVK and PPV-D on ITO substrates with work function ranging from 4.4 to 4.7 eV was investigated. Vacuum level alignment was found to prevail in all cases, with additional band bending in the polymer when the (hole) injection barrier is small (typically less than 0.6 eV). Accumulation of excess holes at the polymer/metal interface, leading to an electric field that moves the HOMO level away from the Fermi level and limits further penetration of charges into the bulk of the film, was proposed to explain this effect. The luminance (quantum) efficiency increase from ~ 0.8 lm/W for single layer structure to ~ 1 lm/W for the lower work function of ITO and ~ 1.2 lm/W for the higher work function of ITO due to the suitable energy level alignment at the anode interface.

References

1. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, "Light-emitting diodes based on conjugated polymers", *Nature* 347, 539-541, (1990).
2. M. Aleksandrova, "Improvement of the electrical characteristics of polymer electroluminescent structures by using spray-coating technology", *Journal of Coatings Technology and Research* 6, (2009).
3. S. E. Shaheen, R. Radspinner, N. Peyghambarian, and G. E. Jabbour, "Fabrication of bulk heterojunction plastic solar cells by screen printing," *Appl. Phys. Lett.* 79(18), 2996-2998 (2001).
4. L. Yan, Y. Gao, "Interfaces in organic semiconductor devices" *Thin Solid Films* 417, 101-106 (2002).
5. H. Vazquez, F. Flores, R. Oszwaldowski, J. Ortega, R. Perez, A. Kahn, "Barrier formation at metal-organic interfaces: dipole formation and the charge neutrality level", *Applied Surface Science*. 234, 107-112 (2004).
6. T.P., Nguyen, P. Le Rendu, N.N. Dinh, M. Fourmigue, C. Meziere, "Thermal and chemical treatment of ITO substrates for improvement of OLED performance" *Synthetic Metals* 138, 229 – 232, (2003).
7. S. O. Djob, J. C. Bernède, N. Kossi, "PVK/Alq3 organic light emitting diodes obtained by evaporation", *Journal of Materials Science: Materials in Electronics* 15, 579-582 (2004).
8. J. W. Lee, J. K. Kim, Y. S. Yoon, "Performance Improvement of Organic Light Emitting Diodes Using Poly(N-vinylcarbazole) (PVK) as a Blocking Layer". *Chinese Journal of Chemistry* 28, 115 – 118, (2010).
9. M. Aleksandrova "Spray Deposition of Multilayer Polymer Structures for Optoelectronic Applications", *e-Journal of Surface Science and Nanotechnology*. 7, 859-862 (2009).
10. D. Cahen, A. Kahn, "Electron Energetics at Surfaces and Interfaces: Concepts and Experiments", *Advanced Materials* 15, 271 -277, (2003).
11. J. Cornil, S. Vanderdonckt, R. Lazzaroni, D. A. dos Santos, G. Thys, H. J. Geise, L.-M. Yu, M. Szablewski, D. Bloor, M. Lo'gdlund, W. R. Salaneck, N. E. Gruhn, D. L. Lichtenberger, P. A. Lee, N. R. Armstrong, J. L. Bre'das, "Valence Electronic Structure of π -Conjugated Materials: Simulation of the Ultraviolet Photoelectron Spectra with Semiempirical Hartree-Fock Approaches", *Chemistry of Materials*, 11, 2436 -2443 (1999).
12. X. Gong, S. Lim, J. C. Ostrowski, D. Moses, Ch. J. Bardeen, G. C. Bazan, "Phosphorescence from iridium complexes doped into polymer blends", *Journal of Applied Physics*. 95, 948-953, (2004).
13. I. G. Hill, A. Kahn, Z. G. Soos, R. A. Pascal, "Occupied and Unoccupied Electronic Levels in Organic p-conjugated Molecules: Comparison Between Experiment and Theory," *Chemistry Physics Letter*. 327, 181-188 (2000).
14. A. N. Caruso, D. L. Schulz, P. A. Dowben, "The physics of solid-state neutron detector materials and geometries," *Chem. Phys. Lett.* 413, 321 (2005).
15. C. Tengstedt, W. Osikowicz, W. R. Salaneck, I. D. Parker, C. H. Hsu, M. Fahlman, "Fermi-level pinning at conjugated polymer interfaces", *Applied Physics Letters* . 88, 053502 (2006).