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Conjugated polymer surfaces and interfaces

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The doping of a conjugated polymer, polyacetylene, to a state of high electrical conductivity in 1977 marked a distinct step in interest in the electronic and transport properties of *electrically conducting* organic materials. Since 1990, however, undoped *semiconducting* conjugated polymers have emerged as potentially useful electronic materials in a variety of electronic and optoelectronic applications. In the context of polymer-based electronic device applications, it is of critical importance to understand the nature of the electronic structure of the polymer surface and the polymer–metal interface. It has been shown that, especially for conjugated polymers, photoelectron spectroscopy provides a maximum amount of both chemical and electronic structural information within a single measurement technique. This contribution contains an overview of some details of the early stages of interface formation with metals on the surfaces of conjugated polymers and model molecular solids, as studied using photoelectron spectroscopy. The materials chosen are especially of interest in connection with polymer-based light emitting devices, or LEDs. Specifically, the materials involved include poly(p-phenylenevinylene), or PPV, and a series of substituted PPVs, as well as a diphenylpolyene molecule for PPV, namely, α, ω-diphenyltetradecaheptaene. Some general trends in the behaviour of light-metal atoms on the clean surfaces of conjugated polymers are pointed out. Some consequences, based upon the information obtained in the studies reviewed, are highlighted. Finally, two recent issues, which are studied by the methods used for the metal-on-polymer interfaces studies, are covered: the role of water vapour on the electronic structure of PPV; and the use of phase-separated polymer blends to increase the quantum efficiency of blue light emitting diodes.

1. Introduction

One of the recent breakthroughs in the field of semiconducting π-conjugated polymers (Brédas & Silbey 1991; Stafström *et al.* 1993; Salaneck *et al.* 1993; Salaneck & Brédas 1994) is the discovery at the University of Cambridge (Burroughes *et al.* 1990; Friend 1993) that poly(p-phenylenevinylene), or PPV, and related polymers, may be used as the active media in polymer-based light-emitting devices (Bradley & Tsutsui 1995; Braun & Heeger 1982; Burn *et al.* 1992, 1993; Gill *et al.* 1994; Grem *et al.* 1992; Gustavsson *et al.* 1992; Halliday *et al.* 1993; Ohmori *et al.* 1991a, b; Parker 1994; Brédas & Salaneck 1995), otherwise denoted polymer-LEDs. The chemical structure of PPV is shown in figure 1. In addition to a high photo-luminescence quantum efficiency, ultra-thin films of PPV exhibit high electro-luminescence or quantum yield, both in the yellow–green portion of the visible spectrum (Burn *et al.* 1992, 1993; Halliday *et al.* 1993). In addition, other π-conjugated polymers may be used to provide

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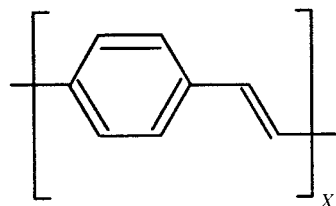790   *W. R. Salaneck*

Figure 1. The chemical structure of poly(*p*-phenylenevinylene), or PPV.

light from somewhat different portions of the visible spectrum. Poly(*p*-phenylene), or PPP, emits in the blue, but with a relatively low quantum efficiency (Grem *et al.* 1992). In addition, emission in the more-or-less red–orange part of the spectrum may be obtained from either a derivative of PPV, namely poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylenevinylene), denoted MEH-PPV (Braun & Heeger 1991; Gustavsson *et al.* 1992; Parker 1994), or from a cyano-substituted PPV, denoted CN-PPV (Greenham *et al.* 1993).

A major factor determining the quantum yield for luminescence is the competition between radiative and non-radiative decay of the electron–hole pairs created within the polymer layer. These pairs can migrate along the chains and are therefore susceptible to trapping at quenching sites where non-radiative (e.g. multiphonon) processes can occur (Friend 1993).

Another factor in determining the overall quantum efficiency of polymer-LEDs is the injection of electrons and holes at the respective metal–polymer interfaces (Bradley & Tsutsui 1995; Parker 1994; Salaneck *et al.* 1996). Typically, but not exclusively, glass, coated with the degenerate semiconductor indium-tin-oxide (ITO), is used as the hole injecting contact. The large optical band gap of ITO allows visible light to escape from the active light-generation medium (Bradley & Tsutsui 1995; Parker 1994). Electron injection into the conduction band of the polymer medium is usually accomplished using a metal with low work function, which is applied to the conjugated polymer surface by physical vapour deposition (PVD). In this context, the injection efficiency of the minority carrier may be one major limiting factor in overall device efficiency.

During the past five years, there has been a concerted combined experiment–theory approach to the study of polymer surfaces and interfaces carried out within a cooperation between the University of Linköping, Sweden, and the University of Mons-Haunaut, Belgium. This combined approach has been applied to a wide variety of π-conjugated polymers and model molecules, as well as to the early stages of metal interface formation. The combined approach provides more information than possible from either the experimental or the theoretical parts alone.

2. Experimental details

The experimental studies were carried out in UHV using polymer samples for which careful determinations of the electronic band structure had been determined previously. Metal atoms were condensed, in steps of approximately one mono-layer equivalent of surface coverage per step, on the surfaces of ultra-thin films of conjugated polymers, or on the surfaces condensed solid films of model molecules chosen for their relationship to conjugated polymers of interest (Brédas & Salaneck 1995; Salaneck *et al.* 1996; Brédas 1995; Lögdlund *et al.* 1996). By studying a relatively large range of molecular and molecular and polymer materials, as well as a relatively

large array of different metal atoms, certain general trends are observed. It may be categorically stated that in all cases studied, the ideal, simple, abrupt metal-on-polymer interface has never been observed. There always exists an interfacial layer between the polymer surface and the vapour-deposited metallic contact. The nature of this interfacial layer is determined by the chemistry induced by the independent metal atoms during the PVD process. The presence of this interfacial layer seems to have been neglected in analysing the results of electronic charge injection at the metal-on-polymer contact in most studies of polymer LEDs reported thus far.

The polymer materials studied have been chosen from among those relevant to polymer-based LEDs. The list of polymer materials includes poly(*p*-phenylenevinylene) (Fahlman *et al.* 1993), poly(2,5-diheptyl-1,4-phenylenevinylene) (Dannetun *et al.* 1994; Fahlman *et al.* 1994), poly(2,5,2′,5′-tetrahexyloxy-8,7′-dicano-diphenylvinylene) (Fahlman *et al.* 1995), which is a CN-substituted PPV, and several alkyl-substituted polythiophenes (Salaneck *et al.* 1988; Lögdlund *et al.* 1989; Lazzaroni *et al.* 1990*a,b*, 1995). In addition, certain molecules were studied in the condensed molecular state as model systems for the conjugated polymers, including a diphenylpolyene model molecule for PPV, namely α,ω-diphenyltetradecaheptaene (Spangler *et al.* 1987; Lögdlund *et al.* 1992, 1993), abbreviated as 'DP7', and a model molecule for the polythiophenes, α-sexithiophene, or α6T (Lögdlund *et al.* 1996). The list of metal atoms includes aluminium, sodium, calcium, potassium, rubidium and lithium. In all cases, experiments were carried out using ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) in ultra-high vacuum ($p \leqslant 10^{-10}$ Torr) (Brédas & Salaneck 1995; Salaneck *et al.* 1996; Lögdlund *et al.* 1996).

3. Theory

In order to extract a maximum amount of electronic structural information from the UPS spectra, large scale computer based quantum chemical calculations are required. For conjugated polymers, the method shown to be particularly applicable is the valence effective Hamiltonian (VEH) calculations (Brédas & Salaneck 1995; André *et al.* 1991; Brédas *et al.* 1982). The VEH method has an excellent record of providing reliable estimates of ionization potentials, bandwidths and bandgaps for a wide variety of conjugated polymers. The geometries used for the VEH calculations are obtained from full molecular-geometry optimizations using the modified neglect of differential overlap (MNDO) or the Austin model 1 (AM1) Hartree–Fock semiempirical techniques. In addition, when appropriate for treating metal atoms or ions, the local spin density (LSD) model has been employed (Fredriksson & Brédas 1993).

4. Summary of studies on the behaviour of metal atoms on conjugated polymer surfaces

Starting with aluminium (Lazzaroni *et al.* 1994), during the initial stages of interface formation, atoms deposited upon essentially oxygen-free surfaces lead to the formation of covalent bonds. The aluminium–carbon bonds occur at the carbon atoms of the α-linkages in polythiophenes (Lazzaroni *et al.* 1994; Dannetun *et al.* 1993) and α6T (Lögdlund *et al.* 1996). The α-carbon atoms bonded to aluminium atoms become sp^3 hybridized. With an aluminium atom on each of the two α-carbon atoms of a given thiophene ring, the ring becomes very quinoid-like. At the sp^3 hybridized

α-carbon atoms, the conjugation along the polythiophene chain is disrupted, alterating the electronic structure of the polymer film at the aluminium-on-polythiophene interface. The generalized case of aluminium on a trimer of polythiophene has been discussed by Boman & Stafström (1992). In addition, the aluminium atoms remain confined in the near-surface region and also form clusters on the surface at room temperatures (Salaneck *et al.* 1996).

Aluminium atoms react with any of the carbon atoms along the polyene portion of the DP7 molecule (Dannetun *et al.* 1992). The carbon atoms with which the aluminium atoms react become sp^2 hybridized, leading to geometric distortions of the polyene portion of the molecule. The aluminium–carbon covalent bonds are localized such that the total ground state energy of the di-aluminium DP7 system is essentially independent of carbon atoms (of the polyene chain). The aluminium is localized to the near-surface region and forms clusters on the surface at room temperature (Salaneck *et al.* 1996).

For the case of PPV (and alkyl-substituted PPV), aluminium atoms react directly with the vinylene-carbon atoms, although slightly more elaborate configurations are possible in MEH-PPV, DMeO-PPV (Lögdlund & Brédas 1994) and CN-PPV (Fahlman *et al.* 1995). A careful study of the surface localization of the aluminium atoms indicated that, although clustering occurs on the surface just as in the case of aluminium atoms on the surfaces on inorganic semiconductors, diffusion takes place into the near-surface region. Although a diffusion depth distribution profile could not be obtained from the measurements, an estimate of the scale of the diffusion was obtained. The aluminium atoms forming covalent bonds with the molecular or polymer systems were localized to the near-surface region within a characteristic length scale on the order of an electron tunnelling distance, i.e. of the order of 20–30 Å. Note that these are not exact numbers; they are, however, indicative of the scale of the interfacial region.

In all cases studied by the present authors and co-workers, sodium diffuses uniformly throughout the polymer or condensed molecular solid film and donates electrons to the π-system, forming Na^+ ions. This leads to the generation of bipolarons and the appearance of bipolaron states in the original energy gap. For the special case of the DP7 molecule, two solitons are generated, which are confined to the (finite sized) polyene portion of the molecule by the phenyl rings which cap the molecule (for environmental stability). These two confined solitons appear formally equivalent to a single bipolaron, with the exception that if the polyene portion of the molecule was infinitely long, the two observed states in the energy gap would coalesce into one degenerate state (Lögdlund *et al.* 1993; Lögdlund & Brédas 1994). In all of the other cases, the two bipolaron states within the energy gap are a consequence of the non-degenerate ground state of the π-system in all works referred to here (Brédas & Street 1985).

In the case of rubidium or potassium on PPV, substituted PPVs or condensed films of DP7, essentially the same behaviour as that of sodium was observed with the exception that, following vapour deposition, longer times were required to obtain equilibrium, leading thereby to somewhat greater detail in the observed spectra than in the case of sodium (Iucci *et al.* 1995, 1996). For potassium, although again very subtle differences occur, essentially the same behaviour as for sodium or rubidium was obtained. Thus for Na, Rb and K, bulk diffusion and n-type doping of the entire polymer or molecular film are observed.

The case of calcium vapour deposited on PPV is of particular interest because of
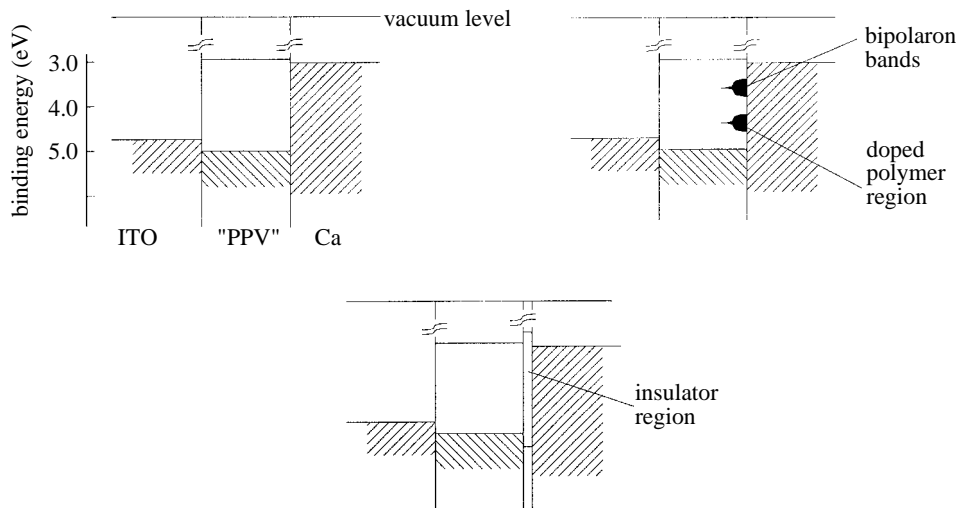
Figure 2. The generalized case of calcium on PPV (on ITO-glass) is illustrated, with alignment of the energy band edges at the vacuum level, in the upper panel. The case of doping of the near-surface region with calcium is shown in the middle panel and the case of an oxide resulting from the presence of oxygen-containing species on the PPV surface is shown in the lower panel (Salaneck *et al.* 1996).

the wide spread use of calcium as an electron injecting metallic contact on PPV-based polymer LEDs. As observed first on *clean surfaces* on DP7 in UHV, and subsequently on *clean surfaces* of DHPPV (Dannetun *et al.* 1994), calcium diffuses into the near-surface region, forms Ca^{2+} ions and donates electrons to the π-system of the polymer. The interfacial region between the calcium contact and the polymer has an approximate scale in the range of 20–30 Å (similar to the case of Al-atoms on PPV). In contrast, in cases where there is a large number of *oxygen-containing species on the surface* of, for example, PPV (Gao *et al.* 1992) or substituted PPVs (Dannetun 1994, personal communication), an interfacial layer, consisting essentially of an oxide of calcium, is formed initially upon the deposition of calcium atoms in UHV. After the oxygen-containing species have been consumed by the initial calcium atoms, subsequent deposition of calcium results in the deposition of calcium metal. The scale of this interfacial oxide (insulating) layer also is of the order of 20–30 Å, depending upon the details of the surface contamination, chemical impurity of the polymer and/or the vapour-deposition environment. The calcium-on-PPV results are summarized in figure 2, where either a doped conducting polymer layer is formed on the oxygen-free surface of PPV (middle panel), or a calcium oxide layer is formed (lower panel) on the surface of PPV containing a large amount of oxygen-containing species (Salaneck *et al.* 1996). Finally, it is important to point out that on oxygen-free surfaces of PPV or CN-PPV, the vapour deposition of calcium in a background pressure of about 10^{-6} mbar of O_2 results in a metallic oxide contact which is observed to increase LED yield, lifetime and luminescence of polymer-based LEDs (Bröms *et al.* 1995).

The consequences of the results outlined above are several. First, in commercial applications, not only is the use of UHV conditions for the deposition of metal (in particular, calcium) not necessary, but UHV is actually detrimental. This is fortunate for future fabrication of polymer-based electronic devices, since UHV conditions would entail increased costs, leading to reduced cost-effective competitiveness of polymer-

based electronics applications. It is likely that control of 'the dirt' in metal contacts, and possibly even in the polymer materials, will be important in the eventual LED device processing. Secondly, in practice, in prototypical devices made today, the surfaces of PPVs (and likely other conjugated polymers) are certainly not totally 'clean', but contain a certain level of oxygen-containing species. It is the presence of these oxygen-containing species, coupled with the fact that typical vacuum systems used to deposit metal electrodes have base pressures of about 10^{-6} mbar, which has made the fabrication of metal–polymer contacts possible in device work carried out to date. The optimum conditions, however, were employed *accidentally*. In future cases, the situation might not be so serendipitous. Thus, the need for careful study and control of the metal-on-polymer interface has been illustrated.

5. Related studies

The tools utilized in the work described above to study conjugated polymer surfaces and interfaces may be applied to related topics important in the area of polymer-based devices. Below, the results of two studies are outlined, both of which are directly related to the area of polymer-based LEDs.

(*a*) *Water in PPV*

There are pronounced effects on the performance of photo-diodes and LEDs caused by the presence of water in PPV (Schenk 1995, personal communication; Friend 1996, personal communication). The effects of water molecules on the electronic structure of PPV have been studied using UPS, XPS and optical absorption spectroscopy (Xing *et al.* 1997). Following the characterization of surfaces of samples of clean PPV, for which the surface oxygen content was less than 1.5at.%, samples were exposed to laboratory air and subsequently examined by XPS and UPS. The presence of a new oxygen containing species (in addition to the unremovable residual oxygen-containing species) was observed in the O(1s) spectrum. In the UPS, the electronic density-of-valence states at the valence band edge was reduced and other features seen to become smeared out. The oxygen containing species could be removed and the original XPS and UPS spectra obtained by heat treatment in UHV for only several hours at temperatures near 200 °C. The absorption–desorption process was completely reversible. Equivalent measurements involving pure O_2 instead of air showed no effects. The culprit was H_2O in the air. Parallel studies using optical absorption spectroscopy showed similar reversible effects. The optical spectra, however, required longer times to return to the original absorption spectrum for PPV, since optical spectroscopy probes bulk properties. The various spectra are not reproduced here (Xing *et al.* 1997).

The effects of the presence of H_2O molecules on the electronic structure of PPV were studied theoretically using several standard quantum chemical methods. The results of these computer simulations (dos Santos *et al.* 1997) indicate that there are three different sites along the PPV chain where H_2O molecules interact, as illustrated in figure 3. The upper and the lower panels in the figure illustrate interactions of the H_2O molecule primarily with the benzene moiety, while the centre panel illustrates the case where the lone pairs of the O-atom in H_2O participate in hydrogen bonding interactions with two H-atoms of the PPV chain, resulting in an increase in the torsion angle between one benzene ring and the vinylene group. The increase in torsion results in a decrease in p_z–p_z overlap between the adjacent carbon atoms
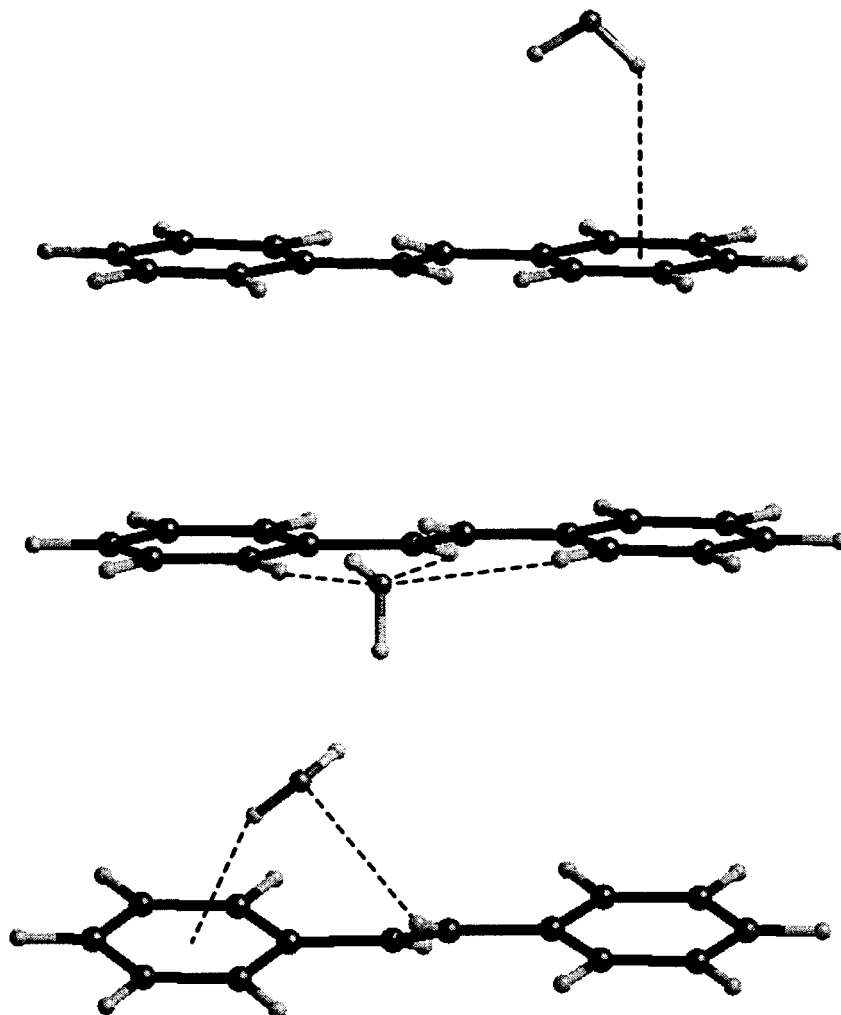
Figure 3. Three different sites along the PPV chain where H_2O molecules interact are illustrated (Xing *et al.* 1997; dos Santos *et al.* 1997).

involved, leading to a decrease in conjugation, opening the HOMO–LUMO band gap. This decrease in conjugation leads directly to the observed decrease in the UPS signal at the valence band edge. The results of this work illustrate the reversible effects of the presence of water molecules on the frontier electronic structure of PPV and a recipe for removing water from PPV in UHV.

(*b*) *Blue LEDs*

An interest in the general behaviour of polymer interfaces, as well as a specific interest in the electronic structure of the strictly alternating copolymer, poly(2,5-diheptyl-1,4-phenylene-alt-2,5-thienylene) (Kaeriyama *et al.* 1996), or PDHPT, lead to the fabrication of a single-layer polymer LED consisting of 'dirty calcium' on PDHPT on ITO/glass (Bröms *et al.* 1995). In order to increase the brightness, devices based upon polymer blends of PDHPT in a soluble substituted-PPP, namely poly(2,5-diheptyl-2′,5′-dipentoxy-diparaphenylene) (Tanigaki *et al.* 1997), or
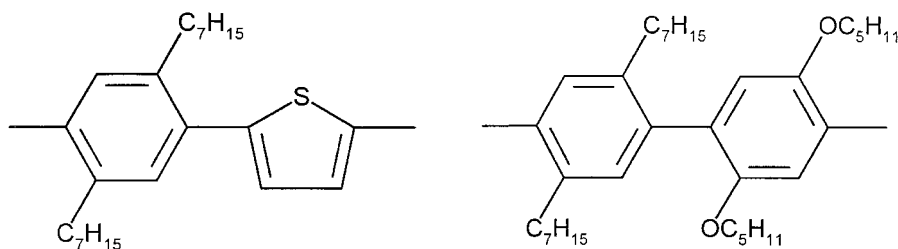
Figure 4. The chemical structure of of PDHPT, poly(2,5-diheptyl-1,4-phenylene-alt-2,5-thi-enylene) (Kaeriyama *et al.* 1996) (left) and poly(2,5-diheptyl-2′,5′-dipentoxy-diparaphenylene) (Tanigaki *et al.* 1997) (right) are shown.
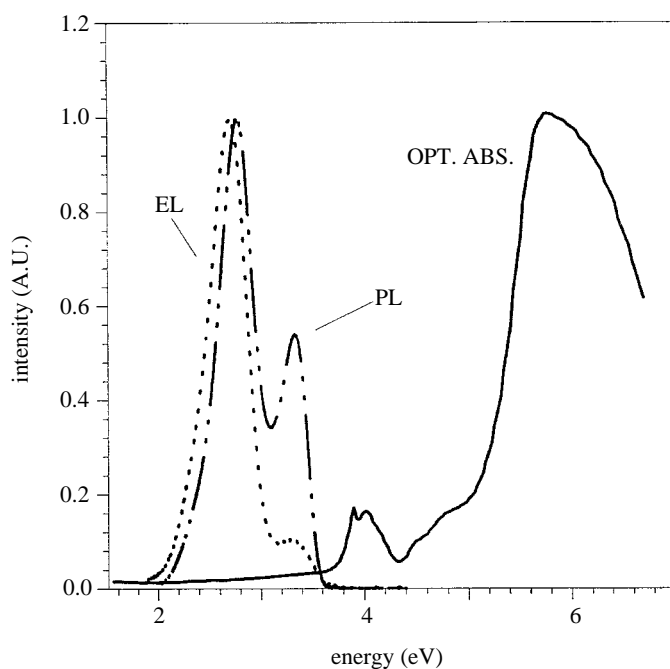

Figure 5. The optical absorption spectrum, the photo-luminescence (PL) and the electro-luminescence (EL) of a device based upon a single layer of 10% PDHPT in PDDPP is shown. The EL is dominated by emission from the PDHPT and the observed external quantum efficiency is about 2% (Birgerson *et al.* 1996).

PDDPP, were studied. The chemical structures of PDHPT and PDDPP are shown in figure 4. Upon varying the starting blend concentration of PDHPT in PDDPP, at a concentration of 10% PDHPT in PDDPP, a maximum in quantum efficiency was observed, the optical spectra of which are shown in figure 5. The key feature of the electronic structure of the polymer blend is illustrated in figure 6. The HOMO–LUMO gap of the guest polymer (PDHPT) is bracketed by the HOMO and LUMO of the host polymer. This relationship among the frontier electronic states leads to trapping sites for electrons and holes, such that the probability of electron–hole recombination is increased. Since it is known that blended polymers will be phase separated on some scale, an interpenetrating inhomogeneously distributed network will be formed. Although, in this particular case, the phase separation scale has not
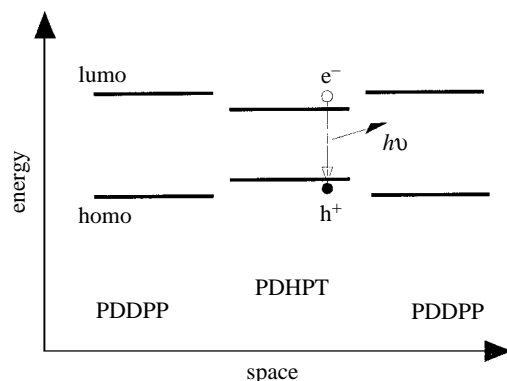
Figure 6. The HOMO–LUMO gap of the guest polymer (PDHPT) is bracketed by the HOMO and LUMO of the host polymer (PDDPP). This relationship among the frontier electronic states leads to trapping sites for electrons and holes, such that the probability of electron–hole recombination is increased.

yet been observed, the fact that an increased quantum efficiency is observed in the electro-luminescence is observed is *de facto* evidence for phase separation.

Figure 4 shows the optical absorption spectrum, the photo-luminescence (PL) and the electro-luminescence (EL) of a device based upon a single layer of 10% PDHPT in PDDPP. The EL is dominated by emission from the PDHPT and the observed external quantum efficiency is about 2%.

The important issues in the polymer blend work illustrate that (1) work on the fundamental properties of materials often lead to opportunities in applications which are unexpected; and (2) a certain degree of 'order' in polymer systems (in this case, the phase separation) can be used to enhance certain electrical properties.

6. Summary

Surface sensitive photoelectron spectroscopy is a tool of choice in studies of the electronic structure of conjugated polymers and the early stages of metal–polymer interface formation. Several issues uncovered have direct and important application in the area of polymer-based light emitting devices. The technique is equally applicable in related problems, as given in one example. Finally, an example is given of the fabrication of one light emitting device with particularly high quantum efficiency, directly as an output of the more basic electronic structural studies of advanced polymer materials.

References

André, J. M., Dekhalle, J. & Brédas, J. L. 1991 *Quantum chemistry aided design of organic polymers.* Singapore: World Scientific.

Birgerson, J., Kaeriyama, K., Barta, P., Bröms, P., Fahlman, M., Granlund, T. & Salaneck, W. R. 1996 *Adv. Mater.* **8**, 982.

Boman, M. & Stafström, S. 1992 *J. Chem. Phys.* **97**, 9144.

Bradley, D. D. C. & Tsutsui, T. 1995 Characterization of the interfaces between low work function metals and conjugated polymers in light emitting diodes. In *Organic electroluminescence.* Cambridge University Press.

Braun, D. & Heeger, A. J. 1991 *Appl. Phys. Lett.* **58**, 1982.

Brédas, J. L. 1995 *Adv. Mat.* **7**, 263.

Brédas, J. L. & Salaneck, W. R. 1995 In *Organic electroluminescence* (ed. D. D. C. Bradley & T. Tsutsui). Cambridge University Press.

Brédas, J. L. & Silbey, R. 1991 *Conjugated polymers.* Dordrecht: Kluwer.

Brédas, J. L. & Street, G. B. 1985 *Adv. Chem. Res.* **18**, 319.

Brédas, J. L., Chance, R. R. & Silbey, R. 1982 *Phys. Rev.* B **26**, 5843.

Bröms, P., Birgersson, J., Johnsson, N., Lögdlund, M. & Salaneck, W. R. *Synth. Met.* **74**, 179.

Burn, P. L., Holmes, A. B., Kraft, A., Bradley, D. D. C., Brown, A. R. & Friend, R. H. 1992 *J. Chem. Soc., Chem. Commun.* **32**.

Burn, P. L., Kraft, A., Bradley, D. D. C., Brown, A. R., Friend, R. H., Gymer, R. W., Friend, R. H. & Jackson, R. W. 1993 *J. Am. Chem. Soc.* **115**, 10117.

Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burn, P. L. & Holmes, A. B. 1990 *Nature* **347**, 539.

Dannetun, P., Fahlman, M., Fauquet, C., Kaerijama, K., Sonoda, Y., Lazzaroni, R., Brédas, J. L. & Salaneck, W. R. 1994 In *Organic materials for electronics: conjugated polymer interfaces with metals and semiconductors* (ed. J. L. Brédas, W. R. Salaneck & G. Wegner), p. 113. Amsterdam: North-Holland.

Dannetun, P., Lögdlund, M., Fredriksson, C., Boman, M., Stafström, S., Salaneck, W. R., Kohler, B. E. & Spangler, C. 1992 In *Polymer–solid interfaces* (ed. J. J. Pireaux, P. Bertrand & J. L. Brédas), p. 201. Bristol: IOP.

Dannetun, P., Boman, M., Stafström, S., Salaneck, W. R., Lazzaroni, R., Fredriksson, C., Brédas, J. L., Zamboni, R. & Taliani, C. 1993 *J. Chem. Phys.* **99**, 664.

Fahlman, M., Salaneck, W. R. & Brédas, J. L. 1995 *Chem. Eur. J.* **3**, 286.

Fahlman, M., Rasmusson, J., Kaeriyama, K., Clark, D. T., Beamson, G. & Salaneck, W. R. 1994 *Synth. Met.* **66**, 123.

Fahlman, M., Beljonne, D., Lögdlund, M., Burn, P. L., Holmes, A. B., Friend, R. H., Brédas, J. L. & Salaneck, W. R. 1993 *Chem. Phys. Lett.* **214**, 327.

Fredriksson, C. & Brédas, J. L. 1993 *J. Chem. Phys.* **98**, 4253.

Friend, R. H. 1993 In *Nobel symposium in chemistry: conjugated polymers and related materials; the interconnection of chemical and electronic structure* (ed. W. R. Salaneck, I. Lundström & B. Rånby), p. 285. Oxford: Oxford Scientific.

Gao, Y., Park, K. Y. & Hsieh, B. R. 1992 *J. Chem. Phys.* **97**, 6991.

Gill, R. E., Malliaras, G. G., Wildeman, J. & Hadziioannou, G. 1994 *Adv. Mat.* **6**, 132.

Greenham, N. C., Moratti, S. C., Bradely, D. D. C., Friend, R. H. & Holmes, A. B. 1993 *Nature* **365**, 628.

Grem, G., Leditzky, G., Ultrich, B. & Leising, G. 1992 *Adv. Mat.* **4**, 36.

Gustavsson, G., Cao, Y., Treacy, G. M., Klavetter, F., Colaneri, N. & Heeger, A. J. 1992 *Nature* **357**, 477.

Halliday, D. A., Burn, P. L., Bradley, D. D. C., Friend, R. H., Gelsen, O. M., Holmes, A. B., Kraft, A., Martens, J. H. F. & Pichler, K. 1993 *Adv. Mat.* **5**, 40.

Iucci, G., Lögdlund, M., Fahlman, M. & Salaneck, W. R. 1995 *Chem. Phys. Lett.* **244**, 139.

Iucci, G., Lögdlund, M., Spangler, C. W. & Salaneck, W. R. 1996 *Synth. Met.* **76**, 209.

Lazzaroni, R., Brédas, J. L., Dannetun, P., Fredriksson, C., Stafström, S. & Salaneck, W. R. 1994 *Electrochim Acta* **39**, 235.

Lazzaroni, R., Brédas, J. L. & Salaneck, W. R. 1997 (Submitted.)

Lazzaroni, R., Lögdlund, M., Calderone, A., Brédas, J. L., Dannetun, P., Fauquet, C., Fredriksson, C., Stafström, S. & Salaneck, W. R. 1995 *Synth. Met.* **71**, 2159.

Lazzaroni, R., Lögdlund, M., Stafström, S., Salaneck, W. R. & Brédas, J. L. 1990a *J. Chem. Phys.* **93**, 6.

Lazzaroni, R., Lögdlund, M., Stafström, S., Salaneck, W. R., Bradley, D. D. C., Friend, R. H., Sato, N., Orti, E. & Brédas, J. L. 1990b In *Conjugated polymeric materials: opportunities in electronics, optoelectronics and molecular electronics* (ed. J. L. Brédas & R. Chance), NATO ASI Series E, vol. 182, p. 149. Dordrecht: Kluwer.

Lögdlund, M. & Brédas, J. L. 1994 *J. Chem. Phys.* **101**, 4357.

Lögdlund, M., Dannetun, P., Fredriksson, C., Salaneck, W. R. & Brédas, J. L. 1996 *Phys. Rev.* B **53**, 16 327.

Lögdlund, M., Dannetun, P. & Salaneck, W. R. 1996 In *Handbook of conducting polymers* (ed. T. Skotheim, J. Reynolds & R. Elsenbaumer). New York: Marcel Dekker.

Lögdlund, M., Dannetun, P., Sjögren, B., Boman, M., Fredriksson, C., Stafström, S. & Salaneck, W. R. 1992 *Synth. Met.* **51**, 187.

Lögdlund, M., Dannetun, P., Stafström, S., Salaneck, W. R., Ramsey, M. G., Spangler, C. W., Fredriksson, C. & Brédas, J. L. 1993 *Phys. Rev. Lett.* **70**, 970.

Lögdlund, M., Lazzaroni, R., Stafström, S., Salaneck, W. R. & Brédas, J. L. 1989 *Phys. Rev. Lett.* **63**, 1841.

Ohmori, Y., Uchida, M., Muro, K. & Yoshino, K. 1991a *Jap. J. Appl. Phys.* **30**, L1938.

Ohmori, Y., Uchida, M., Muro, K. & Yoshino, K. 1991b *Solid State Commun.* **80**, 605.

Parker, I. D. 1994 *J. Appl. Phys.* **75**, 1656.

Salaneck, W. R. & Brédas, J. L. 1994 Special issue on 'Highlights in condensed matter physics and materials science'. *Solid State Commun.* **92**, 31.

Salaneck, W. R., Lundström, I. & Rånby, B. 1993 *Nobel symposium in chemistry: conjugated polymers and related materials; the interconnection of chemical and electronic structure.* Oxford University Press.

Salaneck, W. R., Stafström, S. & Brédas, J. L. 1996 *Conjugated polymer surfaces and interfaces.* Cambridge University Press.

Salaneck, W. R., Inganäs, O., Thémans, B., Nilsson, J. O., Sjögren, B., Österholm, J.-E., Brédas, J. L. & Svensson, S. J. 1988 *Chem. Phys.* **89**, 4613.

Santos, D. A. dos *et al.* 1997 Proc. ICSM-96. *Synth. Met.* (In the press.)

Spangler, C. W., Nickel, E. G. & Hall, T. J. 1987 *Am. Chem. Soc., Div. Polym. Chem.* **28**, 219.

Stafström, S., Salaneck, W. R., Inganäs, O. & Hjertberg, T. 1992 In *Proc. Int. Conf. Synth. Met.*, pp. 55–57.

Tanigaki, N., Masuda, H. & Kaeriyama, K. 1997 *Polymer.* (In the press.)

Xing, K., Fahlman, M., dos Santos, D. A., Parenté, V., Lazzaroni, R., Brédas, J. L. & Salaneck, W. R. 1997 *Adv. Mat.* **8**, 971.