Electronic Structure of Polyparaphenylene Vinylene Copolymers and Derivatives: Aspects Related to Electrolurninescence Characteristics

D. A. dos Santos, C. Quattrocchi and J.L. Brédas

Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires
Université de Mons-Hainaut, Place du Pare 20, B-7000, Mons, Belgium

In this review, we first describe the main characteristics of the electronic structure of poly(p-phenylene vinylene), PPV. We then discuss the properties of regular and statistical copolymers containing segments of PPV and its dimethoxy-substituted derivative, poly(2,5-dimethoxy-1,4-phenylene vinylene), DMeOPPV. Such copolymers have recently been shown to present remarkable electroluminescence properties. In a third part, we analyze the influente on the electronic properties of PPV, of side-chain substitution with simple acceptor (e.g., cyano) and/or donor (e.g., methoxy) groups. We are mostly interested in the values of the bandgaps, ionization potentials, and electron affinities which are electronic parameters of great importance in determining the potential of such polymers for use as active layers in electroluminescent devices.

I. Introduction

One of the major recent breakthroughs in the field of conjugated polymers[1] is the discovery by the Cambridge group[2] that poly(p-phenylene vinylene), PPV, and related polymers can be used as tlie active compcnent in electroluminescent devices, e.g., light-emitting diodes (LED)[2-5]. Previously, most conjugated polymers had been found to exhibit little luminescence, which was mainly due to the presente of effect ve quenching sites, for instance residual doping sites associated to sample preparation. The discovery of a synthesis based on a soluble precursor route has allowed the obtention of PPV films of good optical quality and containing very low concentrations of spin and charge defects[6-8]. Sucli films then present a higli quantum yield for electro- or photoluminescence in the yellow/green portion of tlie visible spectrum[2-9]. Other luminescent semicoiiducting polymer systems have now been exploited to obtain light emission at other wavelengths; among them, we can mention poly(p-phenylene)[5], which emits in the blue, and a derivative of PPV, poly[2-methoxy-5-(2'-ethyl-hexoxy)-l,4-phenylene vinylene], MEH-PPV, characterized by its emission in the red/orange part of

tlie spectrum[4]. Very recently, a color tuning of luminescence lias been achieved by controlling the molecular architecture of the active polymer, namely in regiospecific alkyl-substituted polythiophenes[10]. The molecular structures of these polymers are sketched in Fig.1.

In liglit-emitting diodes, the active polymer layer is sandwiched between a layer of an electron-injecting low-workfunction metal (sucli as calcium or aluminum) and a layer of a hole-injecting metal (such as indium tin oxide or the conducting form of polyaniline, i.e., emeraldine salt)[2-4]. One of the major aspects determining the quantum yield for luminescence is obviously tlie competition between radiative and nonradiative decay of the electron-hole pairs that are created within the polymer layer. In conjugated polymers, the electron-liole pairs take tlie form of polaron-excitons; this means that tlie pairs are bound botli through a local geometry relaxation (hence, the polaron denomination) and through Coulomb effects (exciton)[11,12]. The pairs can migrate along the chains and are therefore susceptible to trapping at quenching sites where nonradiative (e.g., multiphonon) processes can occur. As a result, it is highly desirable to try to control tlie migration of the electron-liole pairs into chain segments where radiative decay could preferably occur. Tliis was

the idea pursued by the Cambridge group when they proposed the use, as active layer, of a copolymer of PPV and poly(2,5-dimethoxy-l,4-phenylene vinylene), DMeOPPV[9,13]. Since the latter compound possesses a lower bandgap (by about 0.3 eV) than PPV, it **was** expected that the electrons and *the* holes would get confined within DMeOPPV segments of the copolymer cliains where they would more readily recombine.
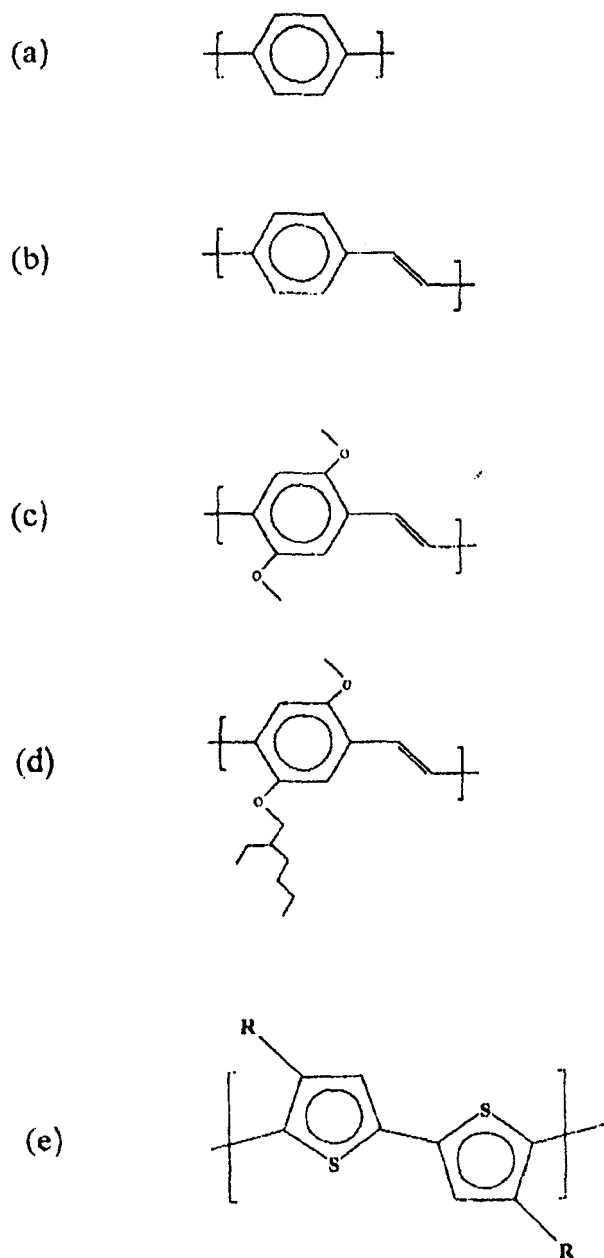

Figure 1: Sketch of the molecular structures of: (a) poly(*p*-phenylene), PPP; (b) poly(*p*-phenylene vinylene), PPV; (c) poly(2,5-dimethoxy-l,4-phenylene vinylene), DMeOPPV; (d) poly[2-*methoxy*,5-(2'-*ethyl-hexoxy*)-l,4-phenylene vinylene], MEH-PPV; and (e) poly(3,3'-dialkyl-2,2'-bithiophene). R represents an alkyl chain.

Another important aspect to achieve high electro-luminescence efficiency is to balance the rates of injection of electrons and lioles from opposite electrodes into the polymer layer[14]. For the conjugated polymers investigated so far, electron injection has proved more difficult tlian hole injection, implying the use of low workfunction metals, such as calcium whose workfunction is ca. 2.9-3.0 eV, in order to obtain good efficiencies, Tlie value of the workfunction for calcium allows to match the electron affinity of a polymer such as PPV, on the order of 2.7-2.8 eV. Nevertheless, calcium is highly susceptible to degradation and difficult to encapsulate, so it is desirable to replace it with metals presenting higher workfunctions (such as aluminum or indium) but displaying greater stability. The workfunction of aluminum is around 4.1-4.4 eV, i.e., more than 1 eV larger than that of calcium. In order for polymer LEDs using aluminum electrodes to provide acceptable efficencies, it is of prime importance to lower the energy of tlie conduction band of the polymer or, in otlier words, to increase its electron affinity. This can be done through side-group substitution of the conjugated polymer backbone with various chemical groups. This approach has been investigated experimentally[15] and theoretically[16].

In this review, we first describe the main characteristics of the electronic structure of PPV. We then discuss tlie results of tlieoretical investigations on the electronic structure of random PPV/DMeOPPV copolymers in order to shed light on the recombination processes in such systems. In tlie following section, we analyze theoretically the influence of PPV side-chain substitution by simple electron acceptor groups, such as cyano group, and/or electron donor groups, such as a methoxy group, on the main electronic parameters, namely the electron affinity (equal to the energy of the bottoni of conduction band), the ionization potential (the energy of the top of the valence band), and tlie bandgap. Our goal is to estimate over wliat range the electronic parameters can be controlled by substitution within the polymer unit cell.

II. Electronic structure of **poly(*p*-phenylene vinylene)**

The electronic band structure of PPV has been described previously on tlie basis of various

techniques[17-21]. PPV can be crudely envisioned as a regular copolymer of polyacetylene, (PA), and poly(*p*-phenylene), (PPP)[17]. Indeed, the characteristics of the PPV π-bands can be analyzed considering the interaction of the π orbitals of the phenylene moieties and those of the vinylene groups, since the unit cell of PPV consists in a styrene unit. As shown in Fig. 2, this leads to dispersed $(\pi_1, \pi_2, \pi_4$ and π_5^* in the figure) and flat $(\pi_3$ and $\pi_6^*)$ s-bands as a function of the symmetry of the original phenylene s levels.
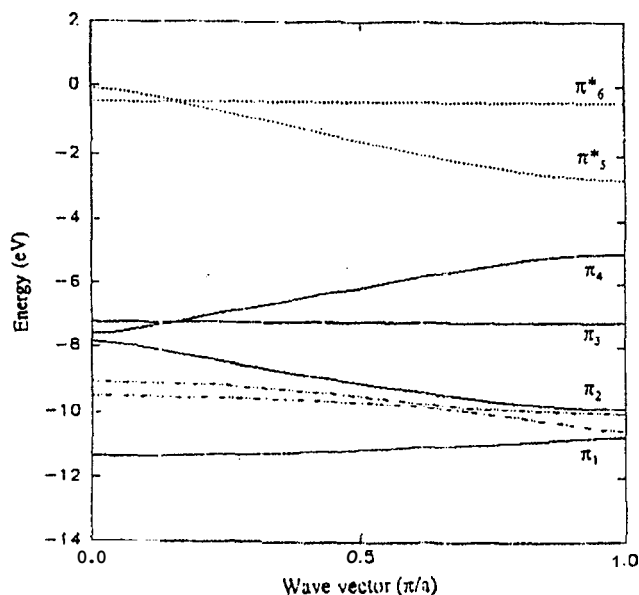

Figure 2: Upper part of the VEH band structure for PPV. Included are some of the unoccupied bands (short dashed lines), all of the occupied π-bands (solid lines), and some of the occupied c-bands (dash-dotted lines).

The bandwidth of the upper occupied r-band (π_4) is about 2.3 eV, when we take into account the avoided band crossing between the π_3 and π_4 bands which occurs near the zone center. Using the valence effective Hamiltonian[22-24] technique, the calculated ionization potential and electron affinity are 5.0 and 2.7 eV, in the solid state, respectively. These values constitute an average of the corresponding values in PPP and PA; the reported ionization potentials for PPP and PA are 5.4 and 4.7 eV and the electron affinities, 2.3 and 3.2 eV, respectively[25]. The bandgap in PPV is then calculated to be **2.3** eV, which is in a good agreement with the optical absorption spectra on well-ordered PPV sample exhibiting the maximum of the first absorption peak at 2.45 eV[20]. A theoretical value of 2.8 eV was recently reported using a local-density-functional band-

structure calculation taking into account the effect of three-dimensional dispersion[21].

III. Copolymers of **poly(*p*-phenylene** vinylene) **and poly**(dimethoxy-p-phenylene vinylene)

The study of the electronic structure of random copolymers presents the additional difficulty of the non-periodicity of the system; the lack of translational symmetry does not allow the use of standard band-structure calculations for this purpose. We have then chosen, for the copolymer calculations, to work with the negative factor counting (NFC) technique, which is appropiate for large non-periodic (macro)molecular systems. The NFC technique is based on Dean's negative eigenvalue theorem[27]. It provides the number of eigenvalues for a real symmetric matrix, which are lower than a given value λ; it uses an algorithm that avoids the direct diagonalization of the full matrix through the use of matrix recursive relations[28]. Applied to the electronic Fock matrix, the method provides the density of the electronic states by varying the λ value over the whole spectrum.

The Fock matrix for the copolymers chains is constructed on the basis of matrix elements coming from valence effective Hamiltonian (VEH) calculations. The VEH method originally proposed by Nicolas and Durand[22] affords one-electron valence levels of ab initio double zeta quality[23,24]. It has an excellent record of providing reliable estimates of ionization potentials, bandwidths, and bandgaps for a wide variety of conjugated polymers. Previous VEH band-structure calculations have allowed for a detailed interpretation of the ultraviolet photoelectron spectroscopy (UPS) spectra of PPV, as well as those of poly(*p*-phenylene) and polyacetylene[17]. Furthermore, the theoretical approach combining NFC and VEH has already been applied successfully to the study of non-periodic conjugated polymers[29,30].

VEH calculations are performed for all the different dimer sequences that can be present along the chains. The geometries used for the VEH calculations are obtained from full molecular-geometry optimizations with the AM1 Hartree-Fock semiempirical technique. For a given concentration of dimethoxyphenylene vinylene vs. unsubstituded phenylene vinylene monomers, non-regular (as well as regular) copolymer chains can be

simulated by choosing a non-periodic (or periodic) disposition of PPV and DMeOPPV sequences. For example, statistical copolymers are studied by using a random generator to set the positions of DMeOPPV units along the chains.
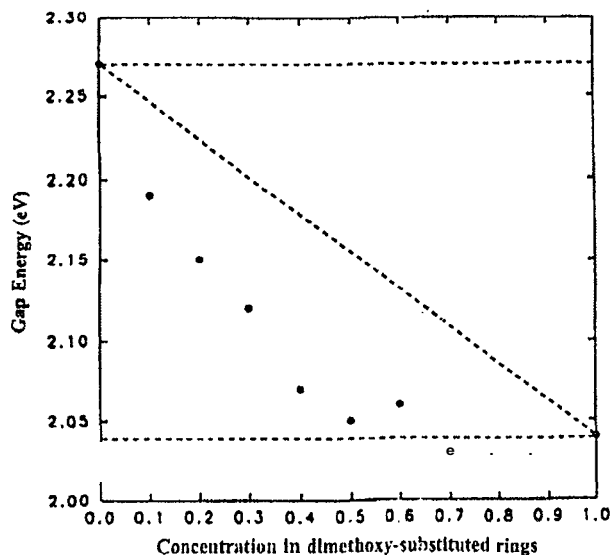

Figure 3: Evolution of the NFC-VEH calculated HOMO-LUMO gap in 100-ring DMeOPPV/PPV copolymer chains, as a function of the concentration in DMeOPPV units. The horizontal dashed lines refer to the homopolymer bandgaps (the top one for PPV; the bottom one for DMeOPPV); the oblique dashed line represents a linear interpolation between the homopolymer bandgaps.

One aspect of major interest in the present electronic-structure calculations is the analysis of the wavefunctions associated to the frontier orbitals [i.e., the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs)]. The energies of these levels can be calculated with any desired accuracy on the basis of the NFC-VEH technique; the corresponding wavefunctions are then obtained using an iterative procedure known as the Inverse Iteration Technique[31]. From the wavefunctions, the degree of spatial localization of the electronic distribution is calculated with the help of the inverse participation number (IPN) approach[32]. For a given electronic levek k, the IPN value I_k expresses the inverse of the number of basis orbitals which participate in the corresponding wavefunction. Thus, the stronger the localization of an electronic level, the larger the IPN value gets, varying from $1/N$ (N=total number of basis orbitals) for a fully delocalized level to 1 for a completely localized state.

We have actually investigated the electronic structure of PPV/DMeOPPV statistical copolymer chains containing 100 arylenevinylene units[33]. In Fig. **3,** we summarize the results for the evolution of the HOMO-LUMO gap as a function of concentration in DMeOPPV units. The evolution of the bandgap values reported by Meyers et al. for stereoregular PPV/DMeOPPV copolymers[25] is also presented. At this stage, it is interesting to note that the substitution with methoxy groups leads to asymmetric destabilizations of the top of valence band and the bottom of the conduction band with respect to PPV, due to the electron donating character of the substituent groups. The ionization potential (IP) decreases by 0.33 eV and the electron affinity (EA) by 0.08 eV when comparing to the PPV values; as a consequence the bandgap is calculated to decrease by 0.25 eV, down to 2.07 eV. This is in excellent agreement with the 2.1 eV bandgap which is measured experimentally[34].
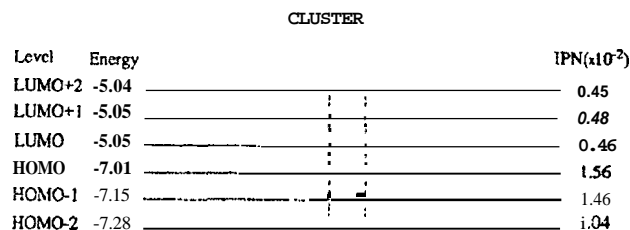

Figure 4: Sketch of the NFC-VEH wavefunctions in the upper three occupied and lower three unoccupied electronic levels for a cluster distribution of a 100-ring DMeOPPV/PPV copolymer chain containing 10% dimethoxy-substituted units. The thin solid lines represent the 100 monomer sites along the chains; the vertical dashed lines mark the locations of the 10 substituted rings; the thick solid lines schematically indicate the localization of the wavefunctions. We also indicate the energies of the levels (in eV) and the associated IPN number.

It is striking that the randomness in the locations of the PPV and DMeOPPV moieties along the chains leads to an evolution in HOMO-LUMO gap which is markedly different from that in the stereoregular chains. In the latter case, the HOMO-LUMO gap value for the copolymers closely follows a linear interpolation between the bandgaps of the parent polymers[25]. For the random copolymers, a small concentration in substituted units provokes a much more significant reduction in the HOMO-LUMO gap, with respect to PPV, than for the corresponding stereoregular chains. For

Table 1: NFC-VEH calculated HOMO-LUMO gaps for the four 100-ring PPV/DMeOPPV copolymer chains containing 10% substituted units.

Distribution	HOMO-LUMO gap (eV)
Regular	2.23
Random A	2.19
Random B	2.13
Cluster	1.99

instance, for *a* statistical copolymer with 10% of substituted units, the reduction in the bandgap values is on the order of 35% of the difference between the parent polymer bandgaps.

The results displayed in Fig. **3** also show a little expected result, that is the consistent appearance, for high DMeOPPV concentration regimes (above 70%), of copolymer HOMO-LUMO gaps *smaller* than that of the homopolymer ones. These results can actually be understood by realizing that the HOMO-LUMO gap is determined not only by the relative concentrations in PPV and DMeOPPV units along the chains, but also by their *relative positions*[33].

In order to precise the influence of relative distributions (positions) in PPV and DMeOPPV moieties on the electronic structure, we have focused our attention on 100-ring copolymer chains presenting the same concentration in substituted units (10%), but differing from one another by distinct arrangements of the DMeOPPV units. In complement to the random distribution for which the HOMO-LUMO gap value is presented in Fig. **3** (which will be referred to as the random-A distribution), we have also considered: (i) another randomly generated configuration (random-B); (ii) a regular distribution in which a substituted ring is located every ten rings (from the fifth ring to the ninety-fifth ring); and (iii) an arrangement where all the substituted rings are kept together in the center of the chain (cluster distribution). The calculated HOMO-LUMO gaps for the corresponding PPV/DMeOPPV copolymer chains are presented in Table 1. Note that random distributions A and B were constructed with the help of a random number generator function as to the locations of the substituted units; a significant difference between them is the occurrence of a segment containing three adjacent DMeOPPV units in distribution B.

From the results displayed in Table **1**, it is clear that the HOMO-LUMO gap in PPV/DMeOPPV copolymer chains is strongly affected by intrachain order. Differences in gap values on the order of 0.24 eV are obtained between the various chain configurations, i.e., a value even sligtlily larger than the calculated energy difference between the parent polymer bandgaps. In particular, it is remarkable that the cluster distribution leads to a bandgap value of 1.99 eV; this is 0.05 eV smaller than the DMeOPPV bandgap and corresponds to the smallest value among those calculated for PPV/DMeOPPV copolymer chains, no matter the concentration or the locations of the substituted units. It should be stressed that the reduction in gap value is induced by the formation of DMeOPPV islands.

To obtain a better insight into the interplay between intrachain order and the electronic structure of PPV/DMeOPPV copolymers, we have calculated the wavefunctions and IPN values (i.e., electronic localization) for the upper three occupied and the lower three unoccupied electronic levels, in the case of the cluster distribution. A schematic representation of our results is given in Fig. 4. The figure provides a remarkable illustration of the fact that, as soon as there appears a clustering of substituted units, there occurs an increased spatial electronic localization and destabilization of the HOMO level. The upper three occupied levels are localized within the DMeOPPV segment, while the lowest unoccupied levels are extended within the unsubstituted regions of the chain.

The wavefunctions calculated for the cluster distribution constitute an excellent example of the general trend which comes out of our results: *The upper occupied levels of non-regular copolymers are localized within a region of the chain where the local concentration of DMeOPPV units is largest, whereas the unoccupied levels remain smoothly delocalized over the unsubstituted segments.* Recombination of electron-hole pairs would therefore take place not within DMeOPPV segments but at the *interface* between DMeOPPV and PPV segments along the copolymer chains.

IV. Derivatized **poly(*p*-phenylene)** vinylene chains

The calculations on the derivatized PPV chains have been performed in two steps using the methods dis-

cussed above[16]. For each polymer, we first carry out a full AM1 unit-cell geometry optimization. The electronic band structure is then obtained with the help of VEH from the AM1 optimized unit-cell geometry. The polymers under study are sketched in Fig. 5. We note that the geometric structure adopted by PPV in the solid state is a planar conformation[35]. In the following, all the PPV derivatives are therefore considered to be planar.

The results of the electronic-structure calculations are summarized in Fig. 5 and Fig. 6. Side-substitution by cyano electron acceptor groups provokes an overall stabilization of the frontier levels. It is also of interest to evaluate whether this substitution effect is stronger when the cyano group is located on the phenylene or vinylene moieties. Considering monocyano substitution, the stabilization effect is calculated to be twice as big in the latter case: with respect to PPV, substitution on the vinylenes leads to an increase of 0.22 eV for IP and 0.37 eV for EA, while substitution on the phenylenes leads to an enhancement of 0.10 eV for IP and 0.18 for EA. Since the asymmetry in the stabilization of valence and conduction bands is smaller than in the dimethoxy case, the bandgap remains larger than in DMeOPPV: 2.17 vs. 2.24 eV. In agreement with chemical intuition, these results and those discussed in the previous section indicate that the methoxy donors have a more significant impact on the valence band edge, while the cyano acceptors affect more strongly the bottom of the conduction band.

The other polymers we have considered are characterized by tlie combination of dimethoxy substitution on the rings and cyano or dicyano substitution on vinylenes[16]. The VEH results for polymer 5 (see Fig. 5}, which is quite similar to the compound recently used by Friend and co-workers[15], indicate a strong stabilization of the conduction band, resulting in an electron affinity which reaches 3.15 eV. This value is 0.42 eV higher than in PPV and even bigger than in either of the monocyano derivatives discussed above. We have also considered a similar compound 6, wliich is a copolymer of DMeOPPV and polymer 7 (dimethoxy dicyano PPV). In this case, still assuming a planar structure, we calculate a larger electron affinity, 3.34 eV; this should lead to an improved efficiency of electron-

injecting contacts with aluminum. We note that polymer 7 is characterized by an even larger value of EA (3.63 eV); nevertheless, the increase in IP is more pronounced than that calculated for copolymer 6. Since this result can affect the hole-injection process, copolymer 6 can be considered as tlie best compound among those discussed here, to be used as an LED active layer.

Relative to PPV, the valence and conduction band edges in the methoxy-cyano derivatives are stabilized. This indicates that in the methoxy-cyano PPV derivatives, the band edges are mostly dominated by the influente of the cyano groups. The fact that the conduction band edge stabilization is much more pronounced than that for the valence band edge results in a strong red shift of the bandgaps, below 2 eV.

V. Synopsis

To summarize, we stress that the electronic structure of PPV/DMeOPPV copolymers is strongly affected by the relative concentrations and locations of the parent polymer moieties along tlie chains. For small concentrations in substituted units, a remarkable variation in HOMO-LUMO gap is obtained when passing from stereoregular chains to chains where the DMeOPPV units cluster. A cluster arrangement leads to HOMO-LUMO gaps whicli are smaller than those in the homopolymers and to a spatial electronic localization of tlie HOMO levels within the DMeOPPV clusters. On the contrary, the LUMO wavefunctions spread over the unsubstituted regions. This phenomenon can be responsible for increased electron-hole recornbinations at *interfaces* between PPV and DMeOPPV segments, and consequently for an improvement in tlie efficiency of radiative decay processes.

In tlie case of PPV derivatives, we have shown how the most important electronic parameters can be affected by side-chain substitution with electron donors and/or electron acceptor groups. In particular, the use of combined methoxy and cyano substituents allows for a significant increase in electron affinity, a feature which results in improved efficiency of electron-injection contacts with aluminum[15], while keeping the ionization potential to a reasonable level. The results discussed here provide a better understanding of those aspects of electronic structure wliich are most relevant to electroluminescent polymer applications.
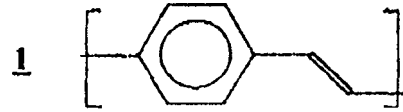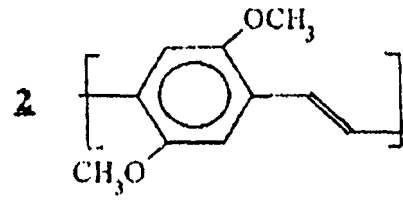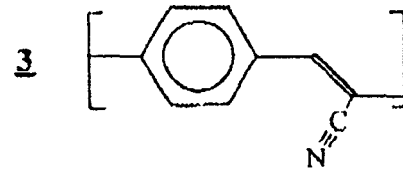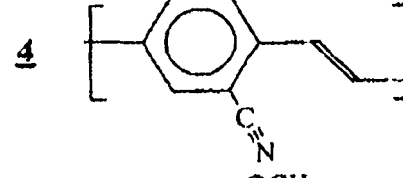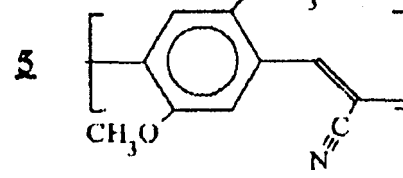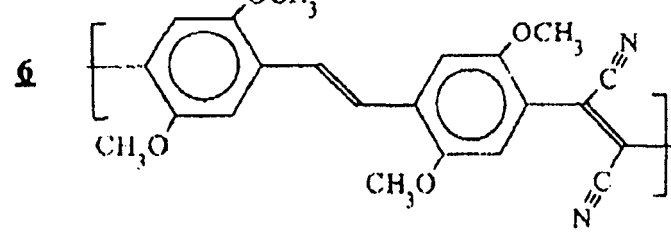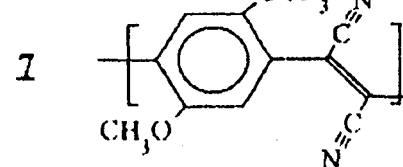
	E_g	IP	· EA
1	2.32	5.05	2.73
2	2.07	4.72	2.65
3	2.17	5.27	3.10
4	2.24	5.15	2.91
5	1.97	5.12	3.15
6	1.74	5.08	3.34
7	1.63	5.26	3.63

Figure 5: Left: Sketch of the molecular structures of some representative polymers: poly(p-phenylene vinylene), 1; poly(2,5-dimethoxy-p-phenylene vinylene), 2; poly(8-cyano-p-phenylene vinylene), 3; poly(2-cyano-p-phenylene vinylene), 4; poly(2,5-**dimethoxy-8-cyano-pphenylene** vinylene), 5; poly(2,5,2',5'-tetramethoxy-7,8-dicyano-di-p-phenylene vinylene), 6; poly(2,5-dimethoxy-7,8-dicyano-p-phenylene vinylene), 7. Right: VEH values (in eV) for: bandgap, E$_g$; solid-state ionization potential, IP; and electron affinity, EA.
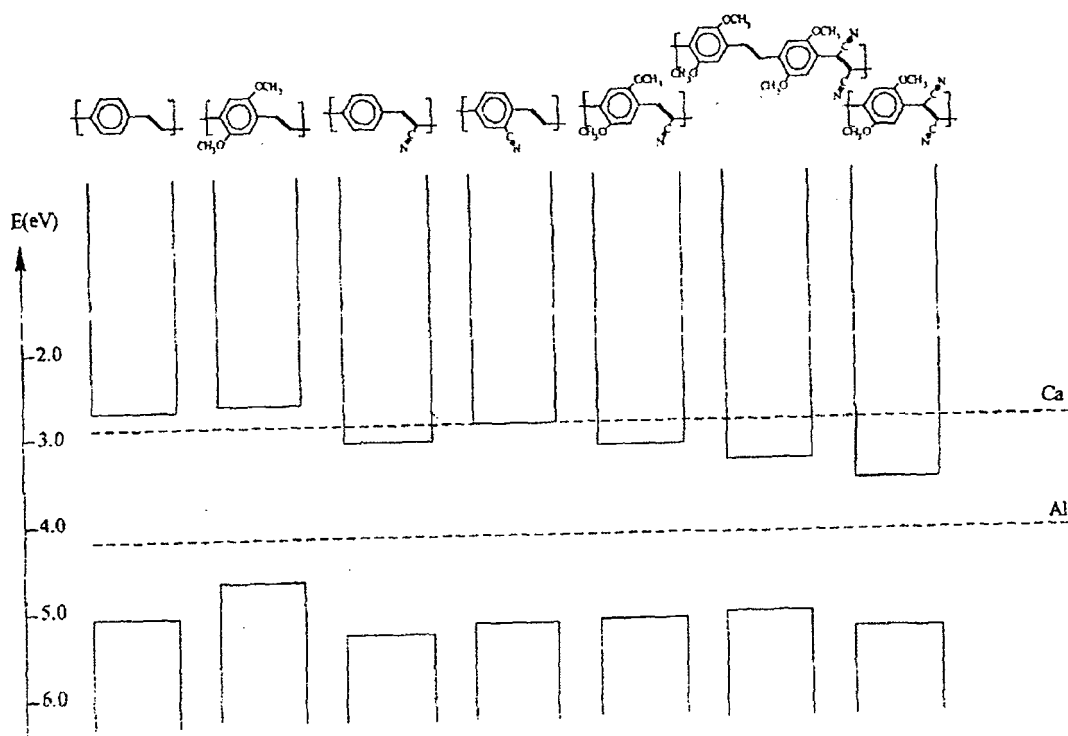
Figure 6: Sketch of the VEH band structures for the polymers of Fig. 5, relative to the workfunctions of calcium and aluminum.

References

1. (a) T. A. Skotheim, ed., *Handbook of Conducting* Polymers, Vols. I and II (Dekker, New York, 1986); (b) J. L. Brédas and R. Silbey, eds., *Conjugated* Polymers (Kluwer, Dordrecht, 1991).

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

3. P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown and R. H. Friend, J. Chem. Soc. Chem. Cornmun. 32 (1992).

4. D. Braun and A. 3. Heeger, Appl. Phys. Lett. 58, 1982 (1991); G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger, Nature 357, 477 (1992).

5. G. Grem, G. Leditzky, B. Ultrich and G. Leising, Adv. Mater. 4, 36 (1992).

6. D. D. C. Bradley, J. Phys. D20, 1389 (1987).

7. T. Murase, T. Ohnishi, T. Noguchi and M. Hirooka, Polym. Commun. 25, 327 (1984); Synth. Met. 17, 639 (1987).

8. F. F. Karasz, J. D. Capistran, D. R. Gagnon and R. W. Lenz, Mol. Cryst. Liq. Cryst. 118, 327 (1985).

9. P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend and R. W. Gymer, Nature 356, 47 (1992).

10. R. E. Gill, G. G. Malliaras, J. Wildeman and G. Hadziioannou, Adv. Mat 6, 132 (1994).

11. S. A. Brazovskii and N. N. Kirova, Pi'sma Zh. Teor. Fiz. 33, 6 (1981) [JETP Lett. 33, 4 (1981)].

12. Z. Shuai, J. L. Brédas and W. P. Su, Chem. Phys. Lett, in press.

13. P. L. Burn, D. D. Bradley, A. R. Brown, R. H.

Friend, D. A. Haliday, A. B. Holmes, A. Kraft, and J. H. F Martens, in *Electronic Properties of Conjugated Polymers IV,* H. Kuzmany, M. Mehring and S. Roth, eds., Springer Series in Solid State Sciences 107, 293 (1992); P. L. Burn, A. Kraft, D. D. C. Eradley, A. R. Brown, R. H. Friend, R. W. Gymer, A. B. Holmes and R. W. Jackson, J. Am. Chem. Soc. 115, 10117 (1993).

14. I. D. Parker, J. Appl. Phys. 75, 1656 (1994).

15. N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend and A. B. Holmes, Nature 365, 628 (1993).

16. J. L. Brédas and A. J. Heeger, Chem. Phys. Lett. 217, 507 (1994).

17. M. Logdlund, W. R. Salaneck, F. Meyers, J. L. Brédas, G. A. Arbuckle, R. H. Friend, A. B. Holmes and G. Froyer, Macromolecules **26,** 3815 (1993).

18. Z. G. Soos, S. Ramasesha, D. S. Galvão and S. Etemad, Phys. Rev. B 47, 1742 (1993).

19. H.-Y. Choi and M. J. Rice, Phys. Rev. B 44, 10521 (1991).

20. P. Gomes da Costa, R. Dandrea and E. M. Conwell, Phys. Rev. B 47, 1800 (1993).

21. P. Gomes da Costa and E. M. Conwell, Phys. Rev. B 48, 3993 (1993).

22. G. Nicolas and Ph. Durand, J. Chem. Phys. 70, 2020 (1972); 72, 453 (1980).

23. J. M. André, L. A. Burke, J. Delhalle, G. Nicolas and Ph Durand, Int. J. Quant. Chem. Quant. Chem. Symp. 13, 283 (1979).

24. J. L. Brédas, R. R. Chance, R. Silbey, G. Nicolas and Ph. Durand, J. Chem. Phys. 75, 255 (1981); J. L. Brédas, in. Ref. 1a. p. 859.

25. F. Meyers, A. Heeger and J. L. Brédas, J. Chem. Phys. 97, 2750 (1992).

26. D. A. Halliday, P. L. Burn, D. D. C. Bradley, R. H. Friend, O. M. Gelsen, A. B. Holmes, A. Kraft, J. H. F. Martens and K. Pichler, Adv. Mater. 5, 40 (1993).

27. P. Dean, Proc. Roy. Soc. London Ser. **A** 254, 507 (1960); Rev. Mod. Phys. 44, 127 (1972).

28. R. S. Day and F. Martino, Chem. Phys. Lett. 84, 86 (1981).

29. D. S. Galvão, D. **A.** dos Santos, B. Laks and M. C. dos Santos, Synth. Met. 43, 3521 (1991).

30. D. A. dos Santos and J. L. Brédas, J. Chem. Phys. 95, 6567 (1991).

31. J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon, Oxford, 1965).

32. R. J. Bell, D. Dean and D. C. Hibbins-Butler, J. Phys. **C 3,** 2111 (1970).

33. D. A. dos Santos, C. Quattrocchi, R. H. Friend and J. L. Brédas, J. Chem. Phys. 100, 3301 (1994).

34. M. Fahlman, M. Logdlund, S. Stafstrom, W. R. Salaneck, S. C. Graham, R. H. Friend, P. L. Burn, A. B. Holmes, K. Kaeriyama, Y. Sonoda, O. Lhost, F. Meyers and J. L. Brédas, submitted for publication.

35. G. Mao, J. E. Fischer, F. F. Karasz and M. J. Winokur, J. Chem. Phys. 98, 712 (1993).