Direct Determination of the Exciton Binding Energy of Conjugated Polymers Using a Scanning Tunneling Microscope

S. F. Alvarado* and P. F. Seidler
IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

D. G. Lidzey and D. D. C. Bradley
Department of Physics, University of Sheffield, Sheffield S3 7RH, United Kingdom

(Received 27 February 1998)

We report scanning tunneling spectroscopy measurements of the threshold energy for injecting electrons or holes into thin, conjugated polymer films deposited on Au(111) substrates. Combining these results with optical absorption measurements, we estimate an exciton binding energy of $E_b = 0.36 \pm 0.10$ eV for poly[(2-methoxy-5-dodecyloxy)-1,4-phenylenevinylene-*co*-1,4-phenylenevinylene] and $E_b = 0.30 \pm 0.10$ eV for poly(9,9'-dioctylfluorene). In addition, we determine the alignment of the electronic levels of the polymers relative to the substrate. [S0031-9007(98)06767-2]

PACS numbers: 73.61.Ph, 71.35.Cc, 71.38.+i, 73.40.Gk

Organic light-emitting diodes (OLEDs) based on polymeric materials are of great interest from both technological and theoretical standpoints. The determination of the electronic levels and excitations is a key factor in understanding the nature of charge injection into the polymers and the subsequent transport and recombination mechanisms. This knowledge will be useful for the design and fabrication of highly efficient devices.

Conjugated polymers are macromolecular semiconductors owing to their electronic π and π^* states delocalized along the polymer backbone. The addition of an electron or hole to a vacant molecular state causes the formation of a polaron, where a local deformation of the polymer occurs around the charge, resulting in a change of bond lengths. This, in effect, moves the polaron energy levels into the HOMO-LUMO gap [highest occupied molecular obital (HOMO), lowest occupied molecular orbital (LUMO)]. It has been argued [1] that, in an OLED, the lowest molecular states into which injection from the metallic contacts occurs are polarons. In this scenario, the polymer chain spontaneously deforms by means of quantum zero-point fluctuations in energy, which prepare the appropriate molecular conformation and vacant state to accept an electron or hole.

The combination of a hole polaron and an electron polaron (P^+ and P^-, respectively) results in the formation of an exciton. The exciton binding energy has been defined [2] as $E_b = E_{g,s} - E_a$, where $E_{g,s}$, the difference between the electron and hole polaron energies, is called the single-particle energy gap [3] and E_a is the energy required to create a molecular exciton. The value of E_a can be determined from optical absorption spectra. Supplying the exciton with energy E_b gives rise to the creation of a pair of oppositely charged polarons. In an OLED, the radiative decay of a singlet exciton results in the emission of a photon. The singlet exciton binding energy for the commonly used material poly(1,4-phenylenevinylene) (PPV) and its derivatives has been determined by a number of different techniques, and values of between 200 and 400 meV have been obtained [3–7]. Other measurements, however, have suggested values as low as 25 meV [8] or as high as about 1 eV [9,10].

In this Letter we report on experiments performed using a scanning tunneling microscope (STM) to determine directly the energies, relative to the Fermi energy of the metallic substrate, at which electrons or holes can be injected into conductive states within the conjugated polymer. By combining the results with measurements of the exciton creation energies, we have been able to determine the exciton binding energies of two different polymers, and find good agreement with other, less direct methods. The spectroscopy technique presented here allows us to probe the density of states in a manner that differs from the frequently used current-voltage spectroscopy technique, where changes in the tunneling current are ascribed to changes in the density of states [11]. Our measurements are taken while the STM feedback loop is active, i.e., at constant tunneling current, so the density of states is probed through the relative tip height as a function of V_T, the potential of the tip with respect to the gold substrate. This technique has recently been used to determine the alignment of the LUMO level of thin films of *tris*(8-hydroxyquinolato)aluminum (Alq$_3$) [12] and, in combination with the luminescence excited by the tunneling current, of poly(1,4-phenylenevinylene) relative to the Fermi level of Au(111) substrates [13]. Note that this application uses an STM as a unique local tool to determine the alignment of the states in organic compounds to the Fermi levels of the anode and cathode materials typically used in devices. This is significant, given that the assumption of a common vacuum level may not be applicable [14,15].

The chemical structures of the conjugated polymers studied in these experiments are shown as insets of Fig. 1.

0031-9007/98/81(5)/1082(4)$15.00

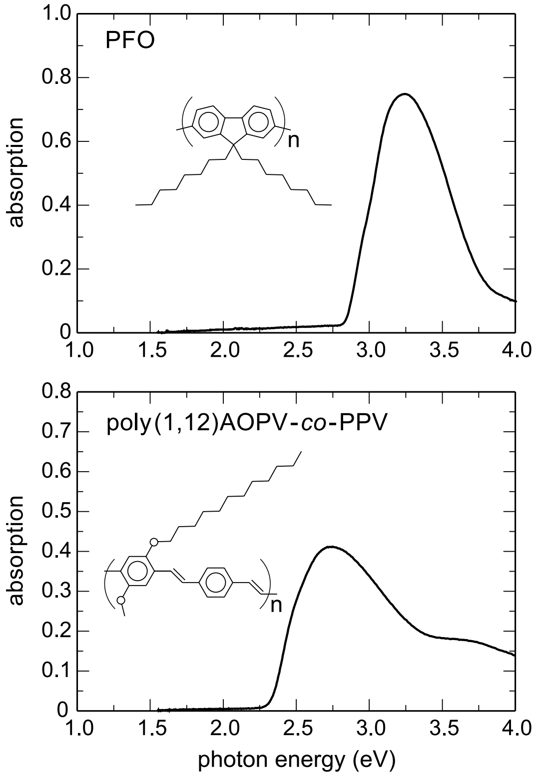

FIG. 1. Optical absorption spectra and structure of the polymers used in this study.

Poly[(2-methoxy-5-dodecyloxy)-1,4-phenylenevinylene-*co*-1,4-phenylenevinylene] [poly(1,12)AOPV-*co*-PPV], a yellow-orange emitter, and poly(9,9'-dioctylfluorene) (PFO), a blue emitter, are used as the active emissive material in OLED devices. Poly(1,12)AOPV-*co*-PPV is an alternating copolymer, and, because of their long aliphatic side chains, both materials are expected to be amorphous. The absorption spectra, Fig. 1, were measured in air using a commercial UV–visible spectrometer on samples made by spin coating a solution of the polymer onto quartz disks to form films of 60 and 100 nm thickness.

The STM system was designed and built in house, and all experiments were performed at room temperature in ultrahigh vacuum (UHV). The polymers were deposited via spin-coating dilute solutions (10 mg/mℓ) onto thin gold films on mica substrates. The thickness of the polymer films was in the range of 2–12 nm. Prior to coating, the gold was cleaned by Ne-ion bombardment and annealed to temperatures of 250 to 300 °C under UHV conditions to produce clean, atomically flat Au(111) terraces. Total exposure of these samples to atmosphere was approximately 30 min. For additional experimental details see Ref. [13]. The bias voltage was ramped while scanning the PtIr STM tip over a small area of the surface (usually 5×5 mm^2) at constant current (15 to 100 pA). Over such a small area, the polymer and the underlying substrate were very flat, allowing variations in the tip height to be ascribed to the electronic properties of the materials alone. Scanning rather than taking the measurement at a point considerably reduced experimental noise. In a typical experiment, the voltage ramp started at a high bias (e.g., 3.0 V) and decreased in 20-mV steps to 0.1 V. Measurements where the ramp runs from low to high bias were also performed. Hysteresis effects were negligible. The data presented are typical of a large set of measurements made at different locations on the sample. The results therefore represent an average sampling of the polymer morphology.

We find that, at a tip bias such that the Fermi level of the tip E_F' lies within the HOMO-LUMO gap, it is not possible to tunnel into states of the polymer, and that the tip penetrates the organic film until charge can tunnel into the substrate [Fig. 2(a)]. Thus, atomically flat Au(111) surfaces can be imaged at low bias (e.g., 0.1 V) even when coated with organic materials [12]. By increasing the magnitude of the tip bias such that E_F' lies above the LUMO state, electrons can be injected into the polymer [Fig. 2(b)], and the surface of the organic material can be imaged instead [12,16]. Similar arguments hold for the HOMO and the injection of holes. Hence when E_F' crosses the threshold for electron or hole injection into the polymer, the tip rises above the surface of the

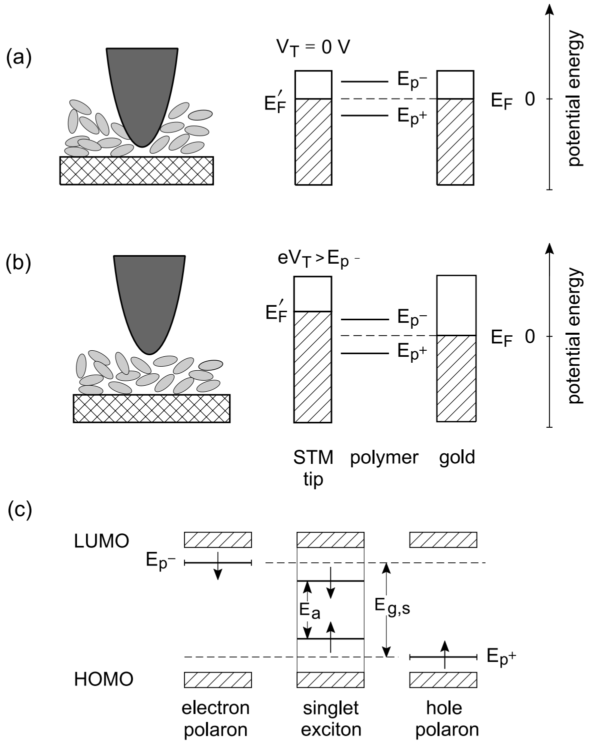

FIG. 2. (a) At small negative tip bias, electrons from the Fermi level E_F' of the STM tip can only access vacant states above E_F of the gold substrate. Under these conditions, the STM tip penetrates the polymer layer and images the underlying gold. (b) As the tip bias is made more negative, electrons can eventually tunnel into vacant states in the polymer, and the tip images the polymer surface instead. Similar arguments apply for reverse polarity. (c) Schematic of polaron energy levels. Combination of polarons with opposite charge and spin forms a singlet exciton.

substrate by a distance corresponding approximately to the thickness of the organic layer. Repeated scanning at low bias followed by topographic imaging at high bias demonstrated some evolution in the distribution of the organic material owing to interactions with the tip. Therefore it appears that the materials studied are soft and mobile enough to be displaced by the tip and are able to rewet the substrate surface even after the tip has completely penetrated the layer.

Figures 3(a) and 3(b) show typical measurements of the relative STM tip-surface separation as a function of the tunneling voltage V_T for films of the two polymers studied. For PFO we find that at low positive tip-bias voltages (between 0.3 and 1.4 V), the tip-surface separation increases with increasing bias at a rate that is characteristic of the clean Au(111) surface. As the bias voltage approaches a threshold value, the tip-surface distance increases in a stepwise fashion, with the tip moving away from the surface by a distance approximately equal to the thickness of the organic material, about 2.0 nm for this sample. In addition, we observe an associated increase in the junction noise. The transition occurs over a few 100 mV for PFO. For poly(1,12)AOPV-*co*-PPV it is less pronounced. Control measurements with uncoated gold surfaces showed that the tip-surface separation increases gradually with increasing voltage, with a maximum increase of approximately 0.6 nm over the bias range of 0.3 to 3 V. Therefore the step threshold, which we determine by linear extrapolation, marks the onset of charge carrier conductance via P^+ states (rather than tunneling through a dielectric). Similar behavior is observed for negative tip bias, allowing the position of the P^- level to be determined.

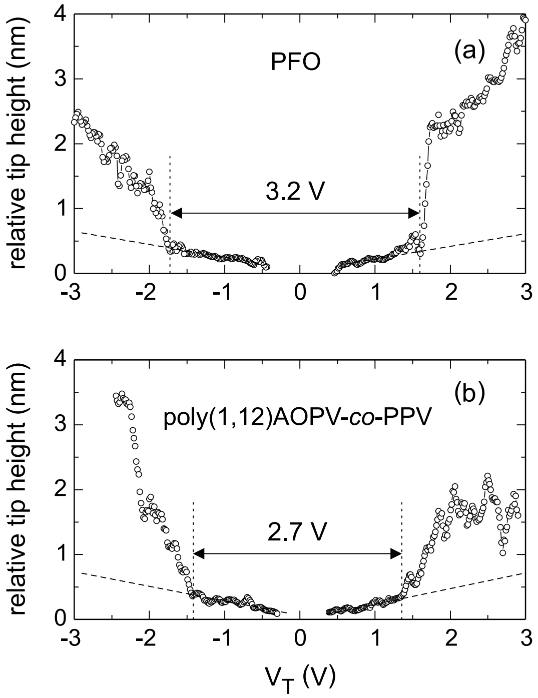

FIG. 3. Typical relative tip height vs tip voltage for (a) PFO ($i_T = 100$ pA for the positive branch and $i_T = 50$ for the negative branch) and (b) poly(1,12)AOPV-*co*-PPV ($i_T = 50$ pA) thin films deposited on Au(111).

From a series of independent measurements, the threshold for injection of holes into PFO was found to be $E_{P^+} = -1.50 \pm 0.05$ eV, whereas the threshold energy to inject electrons is $E_{P^-} = 1.70 \pm 0.05$ eV (referenced to the Fermi level of the substrate). The difference between these two energies yields $E_{g,s} = 3.20 \pm 0.10$ eV for PFO. To explore whether the current density affects the conductance of the polymer, for example, because of filling of trapping levels, measurements were also performed at a tunneling current as low as 15 pA. No effect on the thresholds for charge carrier injection was detected. This is consistent with the interpretation that the steps observed in Fig. 3 reflect the polymer film thickness.

For poly(1,12)AOPV-*co*-PPV we find $E_{P^+} = -1.3 \pm 0.10$ eV, $E_{P^-} = 1.35 \pm 0.05$ eV, and $E_{g,s} = 2.65 \pm 0.10$ eV. The threshold for electron injection into this material is slightly lower than that obtained for unsubstituted PPV on Au substrates [13] and compares reasonably well with values of the barrier height measured by internal photoemission for dialkoxy-PPV/Au [15] and PPV/Au [17] interfaces.

These results allow us to comment on the traditional rule of a common vacuum level often used to determine the alignment of energy levels in multilayer devices. For poly(1,12)AOPV-*co*-PPV, no data is available regarding its ionization potential (IP). However, we are able to estimate the range in which it must lie based on the IP of closely related materials. For PPV-type polymers with dialkoxy substituents on every phenyl ring, such as poly[2-methoxy-5-(2-ethylhexoxy)-1,4-phenylenevinylene] (MEH-PPV), the IP is 5.0 eV [18], and for poly(2,5-dinonyloxy-1,4-phenylvinylene) (NO-PPV), the IP is 4.9 eV [19]. The unsubstituted polymer PPV has an IP of 5.2 eV, although values as large as 6.2 eV have been measured by uv photoelectron spectroscopy [20]. The larger IP value of PPV is not surprising because alkoxy substituents increase the charge density in the π orbitals along the polymer backbone, rendering electrons in the HOMO levels easier to ionize. One would expect that the IP value of poly(1,12)AOPV-*co*-PPV lies between those of PPV and MEH-PPV or NO-PPV, because it has alkoxy substituents on every other phenyl ring. If we assume a common vacuum level, we would estimate that the P^+ level of our PPV derivative is located within several 100 meV of the Fermi level of the Au(111) substrate, which has a work function of $\phi = 5.31$ eV [21]. Similarly, for PFO with IP $= 5.8$ eV and an electron affinity of 2.12 eV [22], we would expect the P^+ level to be 0.5 eV below the E_F of the substrate. Our results, however, show that the Fermi level of Au(111) is located approximately in the middle of the single-particle energy gap. In agreement with internal photoemission experiments [15,17], we conclude that the assumption of a common vacuum level to ascertain the alignment of the HOMO and LUMO levels is not valid. The actual alignment appears to be determined by physical and chemical interactions at the substrate-polymer interface, the nature of which is additionally influenced by atmosphere and solvent exposure. All these effects are neglected in the common-vacuum-level model. Thus, although we may not have examined an ideal interface, our results provide insight into electrode conditions generated in actual OLED fabrication.

In our STM-based experiments, we determine the *threshold* energy for injection of electrons or holes into the P^+ and P^- levels. Combining our data with optical absorption onset data, which gives the energy *threshold* for exciton creation, we calculate $E_b = 0.36 \pm 0.1$ eV for poly(1,12)AOPV-*co*-PPV. This result compares very well with the value $E_b = 0.35 \pm 0.1$ eV for MEH-PPV, which we obtain by taking the single-particle energy gap measured by internal photoemission by Campbell *et al.* [3], and subtracting the optical absorption gap according to the definition given in Ref. [2]. Our result also compares favorably with $E_b = 0.3 \pm 0.1$ eV for PPV, determined from a Monte Carlo study [7]. For PFO, we find $E_b = 0.30 \pm 0.10$ eV. Figure 4 shows a plot of $E_{g,s}$ as a function of the optical absorption edge for the two polymers. It is clear that the energy gap scales with the optical absorption edge of the organic material. There is a small difference in the binding energy between the two conjugated polymers. It is difficult to assess the significance of this observation because the effect of the local chemical environment, polymer morphology, and chain packing on the exciton energy are unknown.

The spectroscopy results described here allow us to probe electronic excitations in conjugated polymers as well as to determine the alignment of the electronic states with respect to the Fermi level of the substrate. The exciton binding energy for the conjugated polymers poly(1,12)AOPV-*co*-PPV and PFO has been determined by taking the difference between the single-particle gap edge and the optical absorption edge (exciton creation threshold). As far as we are aware, this is the first time that such measurements have been performed using an STM. This constitutes a unique local spectroscopic tool which, in principle, can probe the electronic transitions with nanometer spatial resolution. In the future, we hope to use this spatial resolution to explore the homogeneity of the energy-level alignment more extensively.

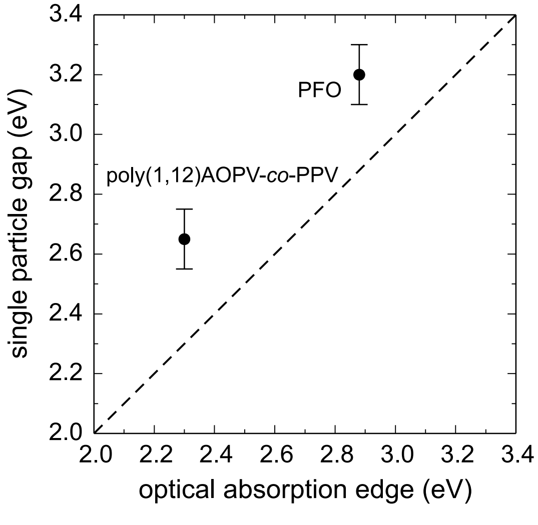

FIG. 4. Single-particle energy gap plotted as a function of the optical absorption edge.

Many thanks to A. Bietsch for providing the Au(111) substrates and to L. Libioulle for fruitful discussions. D. G. L. thanks the Lloyds of London Tercentenary Foundation for support, as well as the Royal Society and the Swiss National Science Foundation for their support, and the Zurich IBM Research Laboratory for hosting his visit. D. D. C. B. gratefully acknowledges the support of a Leverhulme Research Fellowship. We thank E. P. Woo and M. Inbasekaran of the Dow Chemical Company for providing the PFO samples. We also thank P. Bentley, M. Turner, and D. A. Dunmur for the poly(1,12)AOPV-*co*-PPV.

---

*Author to whom correspondence should be addressed.

[1] E. M. Conwell and M. W. Wu, Appl. Phys. Lett. **70**, 1867 (1997); (to be published).
[2] E. M. Conwell, Synth. Met. **83**, 101 (1996).
[3] I. H. Campbell *et al.*, Phys. Rev. Lett. **76**, 1900 (1996).
[4] R. N. Marks *et al.*, J. Phys. Condens. Matter **6**, 1379 (1994).
[5] S. Barth, S. Deussen, and H. Bässler, Philos. Trans. R. Soc. London A **355**, 749 (1997); S. Barth and H. Bässler, Phys. Rev. Lett. **79**, 4445 (1997).
[6] E. L. Frankevich *et al.*, Phys. Rev. B **46**, 9320 (1992).
[7] M. Scheidler *et al.*, Phys. Rev. B **54**, 5536 (1996).
[8] C. H. Lee *et al.*, Phys. Rev. B **49**, 2396 (1994).
[9] J. M. Leng *et al.*, Phys. Rev. Lett. **72**, 156 (1994).
[10] M. Chandross *et al.*, Phys. Rev. B **50**, 14 702 (1994).
[11] See, e.g., R. Feenstra, Phys. Rev. B **50**, 4561 (1994).
[12] S. F. Alvarado, L. Libioulle, and P. F. Seidler, Synth. Met. **91**, 69 (1997).
[13] S. F. Alvarado, W. Riess, P. F. Seidler, and P. Strohriegl, Phys. Rev. B **56**, 1269 (1997), and Refs. 11 and 12 therein.
[14] K. Seki, E. Ito, and H. Ishii, Synth. Met. **91**, 137 (1997); K. Sugiyama *et al.*, Mol. Cryst. Liq. Cryst. **286**, 239 (1996).
[15] G. L. J. A. Rikken *et al.*, Synth. Met. **67**, 115 (1994).
[16] D. G. Lidzey *et al.*, Appl. Phys. Lett. **71**, 2008 (1997).
[17] W. Brüttig *et al.*, Synth. Met. **84**, 677 (1997).
[18] I. D. Parker, J. Appl. Phys. **75**, 1656 (1994).
[19] M. Hamaguchi and K. Yoshino, Appl. Phys. Lett. **67**, 3381 (1995).
[20] N. Sato *et al.*, Chem. Phys. **160**, 299 (1992).
[21] H. B. Michaelson, J. Appl. Phys. **48**, 4729 (1977).
[22] S. Janietz, Fraunhofer Institut für Angewandte Polymerforschung (unpublished).