

Electronic processes at interfaces involving conducting polymers

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Abstract

We present quantum chemical calculations based on self-consistent molecular dynamics to discuss the processes involved in electroluminescence of conducting polymers (especially *trans*-polyacetylene (t-PA)). Specifically addressed are issues of finite and variable chain length, and of the charge transfer needed to make the chemical potential for the polymer and the metal Fermi energy equal, a necessary preliminary to calculations of injection dynamics. We examine the effects of the image interaction of carriers with a metal electrode, including the self-consistent prediction of the bonding pattern. Dynamic calculations include carrier mobilities obtained from computer experiments with an applied electric field, and initial studies of the evolution of two oppositely charged polarons into an exciton. There is a complex link between the behaviour of single polymer chains and descriptions of the polymer as a bulk semiconductor. One significant emerging issue concerns the fraction of polymer molecules contributing to electroluminescence. We comment on what can be learnt about the nature of the contact from scanning probe microscopies. A second major issue concerns the nature of the non-radiative processes competing with luminescence and the way this might be influenced.

Keywords: Electronic processes; Interfaces

1. Introduction

We address here some of the issues relating to conducting polymers in contact with metal electrodes. Some issues relate to the behaviour of the individual polymer strands; other issues concern the description of the ensemble of strands as a bulk semiconductor. It is important to recognize that the polymer strands are not all equivalent: some are shorter, others longer; some strands are more curved or convoluted; others are influenced to some degree by the metal itself, whether chemically or through polarization (the image charge). Thus, there are significant differences from, say, a silicon/metal contact. Differences in the details of the network may underlie observed differences in mid-gap (soliton to band edge) transitions in *trans*-polyacetylene (t-PA), which range from 0.55 eV on polymeric insulators to 0.8 eV on silicon dioxide [1].

One of the differences stems from the finite length of each chain and from the possibility that interchain transfer may be significantly slower than either intrachain carrier motion or the injection step. There is the possibility of effects like the so-called Coulomb blockade

in one of its several forms. This raises the further issue of whether all the polymer strands in an electroluminescent device contribute to the light emission, or whether only a small fraction is able to do so. There are then subsidiary questions as to what makes these strands favoured, if they do exist: is it an enhanced radiative process, or an inhibited non-radiative process? Is this to be controlled by polymer chemistry, polymer texture or, since the roughness of the metal introduces spatial variation in the electric field, by some other parameter like the ratio of polymer strand length to roughness coherence length? The effect of field enhancement by asperities can be linked to experiments in which one metal contact is a scanning tunnelling microscope tip; this method should be especially useful in studies of the injection process itself, and also perhaps to measure differences in the polymer film from one region to another.

2. Theoretical methods

The framework for the understanding of conducting polymers is the Su-Schrieffer-Heeger model [2]. Our

approach takes these ideas further, using molecular dynamics with semi-empirical quantum chemistry at the CNDO (complete neglect of differential overlap) level, as implemented in the Harwell CHEMOS code. Forces on atoms are calculated self-consistently to a chosen degree at each time step; we can include applied fields and, when appropriate (e.g. for a constant temperature ensemble), include additional classical atoms. Our earlier work [3–5] gave results for static and dynamic behaviour of conducting polymers and other systems [6–10], including excited state behaviour. Most of our present results use damped molecular dynamics to provide static equilibria. For the metal contact, we usually assume a simple infinite half-space with a well-defined Fermi level, though we can, and have, made calculations in which the metal chemistry is included within the self-consistent molecular dynamics [5,6]. For insulating polyimide [6] these showed significant chemical interactions, mainly intramolecular charge redistribution, with little charge transfer between metal and polymer.

3. Initial results: the isolated chain

We shall need to estimate the chemical potential for a chain of n carbon atoms and net charge Ne if we are to use Schottky–Mott theory or natural generalizations to predict equilibria in charge transfer between metal and polymer. Suppose the energy of the fully relaxed chain is $E(n, N)$. Then, the work function becomes the arithmetic mean of the electron affinity and ionization potential of this state. We may also use Koopman's approximation to express the work function in terms of the energies of the highest occupied orbital (HOMO) and lowest unoccupied orbital (LUMO), though we usually perform the fuller calculation. For t-PA the two methods agree well for chains of more than about six carbons [5,11].

The work function changes when the net charge on the chain alters, and is reduced by electron injection. For an isolated chain of 20 carbons, for example, the energy ϕ in eV can be well fitted [10] as $-4303.58 + 4.67N + 1.95N^2$. The work function for $N=0$ is 4.67 eV, agreeing well with other methods [12] and with the estimate of 5 eV from $I(V)$ and $C(V)$ data for Schottky diodes [13]. We may also ask: For what value of N does the t-PA chain have the same chemical potential as aluminium (work function 4.28 eV)? This depends on the quadratic term too. About 0.1 electrons need be transferred from aluminium to polymer in this case (for a gold contact, about 0.1 electrons would move from polymer to metal). There are conceptual issues here too; whilst only whole electrons can be transferred to an isolated polymer molecule, a contact might involve states with 0.1 electrons associated with

the atomic wavefunctions of the polymer and the remainder with the metal. We remark that a calculation with only 0.1 extra electrons transferred from metal to polymer shows that the ground state undergoes a significant polaronic distortion (Fig. 1), and this distortion complicates analysis of the carrier injection process. Furthermore, the polymer molecules are unlikely to be straight, and their curvature will affect the work function. For a semicircular t-PA molecule with 20 carbons, the work function from total energies is 0.23 eV higher than for the straight molecule (0.17 eV from the HOMO and LUMO energies).

4. Image effects on the carriers

Most of our results given here relate to straight t-PA chains of 20 carbons normal to a metal surface. Adding an electron gives a polaron-type defect; if it is formed at one end of the chain, it moves towards the centre to lower its energy. Adding a hole yields a polaronic defect too. Unlike some previous simpler models, our self-consistent molecular dynamics gives very similar dimerization patterns in both cases. We can readily include the image interaction with the metal, and this is determined by the distribution of charge associated with carriers on the polymer. For a positive or a negative polaron in t-PA we find [11] a charge alternation on the carbons with amplitude of order $0.05e$, in line with other theories, e.g. [14]. The alternation is consistent with the interpretation [15] of the observed enhanced C(1s) XPS width. Clearly, the spread-out nature of the mobile charge is important,

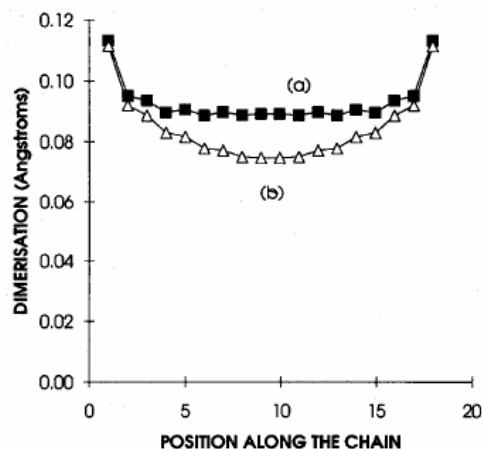


Fig. 1. Dimerization patterns in a t-PA chain with 20 carbons: (a) neutral; (b) after injection of 0.1 electrons. The dimerization is defined [2,3] by the difference in C–C bond lengths at each carbon (e.g. left-hand bond length minus right-hand bond length, so the dimerization changes sign across a soliton).

and crude assumptions (like the polaron charge all being localized at its centroid) are not accurate.

The net effect of the metal is to attract the mobile charge (of either sign), and this shows in the dimerization (Fig. 2). We have added an extra short-range force field to limit motion of the charged chain as a whole towards the metal; this is necessary unless one goes to the greater sophistication of imposing a Fermi wave-vector cut-off on the metal response [16]. For a straight t-PA chain with 20 carbons, the work function is increased by the image interaction by 0.23 eV (total energy estimate; from the HOMO and LUMO energies the effect is only 0.06 eV, the difference coming from the omission of a potential energy term in the one-electron calculation).

5. Key issues

5.1. How many of the polymer strands are involved?

In electroluminescence, an electron injected at one electrode percolates through the polymer film, encounters a hole injected at the other electrode and recombines radiatively or non-radiatively. From the known currents and mobilities, it is clear that there are few carriers present at any one time (for a current 10 i A cm^{-2} , an applied voltage v , a film thickness of $L\text{ }\mu\text{m}$ and a mobility $m \times 10^5\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, there are of order $(iL^2/vm) \times 10^7$ carriers per cm^2 , compared with perhaps $10^{13}\text{--}10^{15}$ polymer strands; even substantial changes in precise numbers do not alter the situation). Some of the polymer molecules may never play a part in the conduction process, whether for topological reasons (connectivity) or because they are inefficient in some basic part of the process. Of these, some small

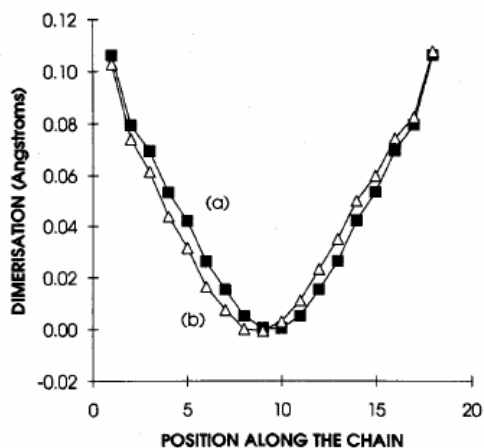


Fig. 2. Dimerization for a negative polaron in t-PA: (a) for an isolated molecule; (b) modified by image interactions with a metal contact.

fraction of the polymer molecules might be responsible for the major part of the light emission. If so, this will not be easy to observe, except perhaps by scanning tunnelling microscopy, since there are many molecules in an area of dimensions of the optical wavelength.

5.2. What limits the charge transferred?

The above discussion of work function implies one limit: charge could be transferred until the chemical potential of the polymer molecule and of the metal are equal. In this picture the charge transfer is limited locally, exactly as in the Coulomb blockade, with the energy change of an individual chain inhibiting the addition of further charges. Precisely what happens in an ensemble of chains of different lengths needs further discussion, especially whether or not charge transfer within the polymer is sufficiently rapid to give a well-defined Fermi level.

There is another limit, recognized in other thin-film processes [17] and grain-boundary behaviour [18] where it is a long-range effect from the electric field of the (possibly delocalized) charge in the film which prevents injection. There can be contributions to this field from charges which have become immobilized on particular strands in the film. We remark that any trapped charge must exceed the typical mobile charge calculated above by several orders of magnitude before its long-range field is likely to have an observable effect. We do not know yet whether this or the local blockade mechanism is the more important; possibly there are regions of the film where one mechanism dominates, and regions where the other dominates.

5.3. Dynamics of the injection process

There are several components of the injection process. One is an electrode process not unlike those for aqueous electrolytes [5]. Here the complexity lies in the fact that the polymer one-electron levels change as the polymer deforms and, hence, as it charges. The calculation requires tunnelling dynamics in conjunction with molecular dynamics. At present, such studies have been limited to far simpler systems [19].

More progress can be made with the dynamical motion of the polaronic carriers once they have entered a polymer strand. We have made separate estimates of the mobilities of the polarons by computer experiments in which their velocity is monitored as a function of applied electric field. For the polarons, our estimates [11] indicate a mobility of order $0.07\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, about an order of magnitude less than our previous estimate for the soliton [4].

We have studied the dynamical behaviour of two polarons (electron and hole; we use the triplet state since this avoids certain technical problems) injected at opposite ends of a t-PA molecule of 42 carbons as

they evolve to become an exciton, and then recombine (Fig. 3). Whilst this is simpler than the real electroluminescent process, it is clear that the exciton formation and recombination steps can be successfully modelled.

5.4. Non-radiative transitions

Possibly the most important obstacle to exploitation of organic electroluminescent films is their efficiency: too much of the electrical energy is converted into heat by non-radiative transitions [20]. Even in traditional semiconductors, it is hard to give quantitative estimates of rates [21,22], but there are useful guidelines. In Ref. [22], experimental data [23] were analysed to identify the mechanism. The conclusion overall was simple: the non-radiative transitions were inhibited when a large number of phonons is needed to take up the energy released, whereas radiative recombination is easier for higher emission energies. If the emission energy is constrained (e.g. by choice of colour) then efficiency can be improved by changes reducing the phonon energies involved. In polymers, these are presumably mainly the C-H vibrations and, unfortunately, they are only modified significantly by isotopic substitution (D

for H). In cases where other modes are important, changes of polymer chemistry may suffice (e.g. F for H, or Si for C).

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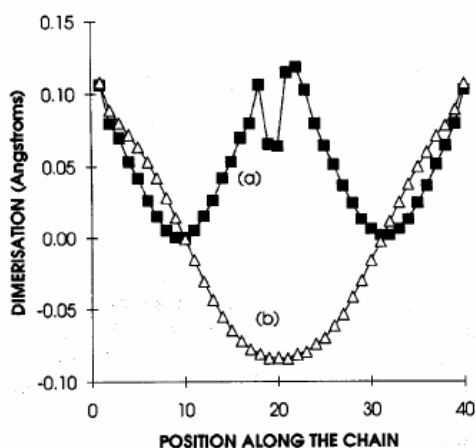


Fig. 3. Evolution of the dimerization pattern in t-PA (chain of 42 carbons): (a) with two oppositely charged polarons; (b) with an exciton.