

Studies of electrochromic devices based on thin films of PProDOT-Me₂

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Abstract

Electrochromic (EC) materials such as poly (dimethyl 3,4- propylenedioxythiophene) show great potential for numerous future applications due to their high change in absorption when their level of doping is varied and fast switching times (on the order of seconds). We have constructed EC devices based on this polymer and conducted spectroscopic measurements in the ultraviolet through far infrared range using both a Fourier Transform Infrared interferometer and a microscope grating photometer. These data are used to determine the contrast between doped and neutral states, the time required for the material to fully oxidize and neutralize, and the lifetime of the device. Our results indicate a maximum change in reflectance between doped and neutral states ($\Delta\%R_{\max}$) of 93% at a wavelength of 1420 nm between doped and neutral states, as well as rapid switching times, but suggest more research is necessary to increase the lifetime to a length appropriate for further use.

1. Introduction

Recent years have seen an increased interest in the ability of certain conducting polymers to undergo a change in reflectance and transmittance properties when an electric potential is applied to them. Known as electrochromism, this ability is basically a change in the absorbance spectra of the polymers due to electronic excitations in the polymer chain caused by a change in dopant level. It is potentially useful in a wide variety of commercial applications, once a material is produced that displays a high magnitude of electrochromic behavior while remaining stable for long periods of time and not breaking down due to the repeatedly applied voltage. Electrically tinted windows and mirrors, low-energy displays, and many other devices based on these electrochromic polymers could be available in the near future. Work must first be done, however, to find a polymer that fits the qualifications and to discover the best way to configure the material for use.

Our group has begun by measuring the spectrum of poly (dimethyl 3,4-propylenedioxythiophene), PProDOT-Me₂ for short, and by testing its suitability for the aforementioned applications. This polymer, shown in Fig. 6, in particular is promising because it shows, at least in the visible range, the greatest contrast between the doped and neutral states among the PProDOT derivatives, increasing its usefulness [1]. We have also looked into different parameters of the electrochromic (EC) cell, such as polymer thickness, and tried to pinpoint factors that cause the polymer film to break down over time. What follows will be a brief introduction to electrochromism and the specific materials used in our experiments, followed by an explanation of our experimental techniques and the results and conclusions we have obtained.

2. Polymer Theory

Conjugated polymers, characterized by a single-bond/ double-bond alternation along the backbone of the polymer, become conductors when “doped,” or infused with ions. Conjugated polymers that have two-fold degeneracy in the ground state are known as degenerate ground state polymers. Polyacetylene is an example of this type [2]. However, the polymers of interest to us are known as non-degenerate ground state polymers, because their ground states are at differing energy levels (not degenerate). Our materials are put into a conducting state by doping, a process in which anions are electrostatically drawn to the polymer when a voltage is applied, producing certain conjugational defects in the chain which cause the interesting EC properties.

These defects, examples of which are shown in Fig. 7, can be solitons (solitary waves), polarons (soliton-antisoliton pairs), or bipolarons (pairs of like solitons). A soliton is simply a lone charge, either an electron or a positive charge. Lone solitons do not appear in thiophene-based polymers, however. A soliton-antisoliton pair, or polaron, is created when a dopant ion draws a positive charge toward it, leaving a corresponding negative charge on the other side of the molecule. This does occur commonly in our materials. When two like charges are unable to move along the molecule, as solitons are typically allowed to do, they form a bipolaron, which may be stable in non-degenerate ground state polymers only [3]. The important point is that these defects are responsible for many EC properties in our materials. Doping the polymer adds intermediate energies in between the valence and conduction bands, which changes its absorption bands (Fig. 8) [4,5]. Part of the research has been to find for which wavelengths absorption increases and for which it decreases. Results will follow later, but for now it is

interesting to note that an increase in absorbance in the visible range can be accompanied by an reduction in the infrared, and vice versa. In short, the effect is not the same throughout the entire spectrum.

3. Experimental Technique

Our samples are synthesized, doped, and deposited into thin films at the same time by electrochemical polymerization. Current is passed through a solution of the component monomers, which causes them to polymerize and collect at the anode. Also dissolved in the solution is LiClO_4 , causing the polymer to be infused with the perchlorate ions at the same time it is synthesized and deposited. Two films are then taken to make each cell. A diagram of the cell is shown in Fig. 1. Glass or ZnSe is used as the window to the cell. The choice depends on which wavelengths are being scanned. Glass is more transmissive than ZnSe in the ultraviolet and visible spectrum, and is used between wavelengths of $0.3 \mu\text{m}$ and $3 \mu\text{m}$. ZnSe retains its transmissiveness much farther into the infrared, from $0.5 \mu\text{m}$ to $20 \mu\text{m}$. The purpose of the electrolyte gel and gold-coated, slitted mylar is to ensure rapid and even switching. The cell is connected to a voltage source, and spectroscopic measurements are taken as one potential is applied, then followed by an oppositely directed potential.

Our studies make use of two instruments, a Bruker 113v Fourier Transform Infrared (FTIR) spectrometer and a Zeiss MPM 800 microscope photometer. The first is an interferometer which scans regions of the spectrum from the near to mid IR, and the second is a grating spectrometer that measures from the lower energies of the ultraviolet to the near infrared. With the former, measurements are taken over the surface of the entire sample. The key difference is that with the microscope one can focus in on a very small area of the sample to test.

This is an advantage because small physical defects that would adversely affect a full-cell scan can be carefully avoided. Also, studies can be done that show which parts of the polymer become damaged first after many cycles of oxidation and reduction.

One of the most important experiments tests the lifetime of the polymer, or how many times it can be oxidized and reduced (or, doped and neutralized) without excessive damage. This knowledge is extremely relevant to future commercial applications. A voltage source is connected which is programmed to change from positive to negative and back every 40 sec. Although there is an immediate change when the potential is switched, this switching period allows a complete oxidation or reduction over the entire surface of the film. The cell undergoes this switching thousands of times, and a reading is taken every 2000 switches. A change in the spectrum that signals damage is a lessening of the reflectance associated with a fresh sample.

Other important experiments include finding the switching time and studying the effect of the electrolyte gel on the spectrum. For the former, graphs of reflectance versus time are very useful; one can measure the time interval between the highest and lowest points of the graph. For the latter, reflectance vs. wavelength is the appropriate plot. Different curves are drawn for each voltage applied to the polymer film, and a very clear contrast is observable.

4. Results

A graph of reflectance vs. wavelength for PProDOT-Me₂ is given in Figure 2. It shows an 84% change in reflectance ($\Delta\%R$) at 1420 nm between voltages of 1.0 V and -1.0 V. Between 1.0 V and -1.5 V, the contrast is as much as 93%. This clearly demonstrates the material's high electrochromicity in the near infrared. $\Delta\%R$ does not seem to remain at such levels as

wavelength increases, however, the two low-reflection regions at 2.8 μm and 3.32 μm are due to water and to C-H stretching in the gel electrolyte, not the polymer sample.

Figure 3 shows a graph of reflectance versus time, taken from FTIR data. Not only does this sort of graph give the $\Delta\%R$ for whichever wavelengths one chooses to plot, but also the graph can be used to find the time required for a full switch to the most contrasting reflectance values. This graph indicates that for a wavenumber of 3850 cm^{-1} ($=2600\text{ nm}$) the total switching time is about nine seconds, three for doping and six for neutralizing; however, the most drastic change in the doping occurs within about one second.

Figures 4 and 5 show the reflectance versus time graphs for both the doped and neutral states. These are the result of the aforementioned lifetime test. Some degradation of the polymer is clearly visible almost immediately after the test begins, but the rate of damage decreases with the number of cycles (oxidation and reduction pairs) completed. By the completion of 1500 deep double potential switches, or cycles, there is only a 7% difference in reflectance, compared to the 90% that was measured at the beginning for the sample in Fig. 4. Figure 5, however, shows a loss of only 20% after 10000 switches. This is due to differences in the samples that are discussed in the next section.

5. Conclusions

The data above show that some aspects of PProDOT-Me₂ make it an ideal material for electrochromic devices, and that some deter its use. Clearly, its usefulness depends on the wavelength for which it is needed. Its use would be limited to a certain spectral range that demonstrates a high contrast in reflectance between states. However, in that range one could

expect that contrast to be quite high. One of our more encouraging findings is the low switching times necessary, which could prove to be of great advantage in future applications.

Of course, contrast and rapid switching do little good if the material begins to break down after a relatively small number of switches. The results show both encouraging and disappointing lifetimes for the EC cell. One explanation for this discrepancy comes from the fact that uneven oxidation and reduction can cause one layer to degrade more rapidly. The degradation of one layer then harms the ability of the other to be switched. If the potentials used were too different in magnitude, damage can be hastened. Differing thickness and surface area can also cause one layer to degrade faster, because only when the same amount of charge is transferred between the same amounts of polymer arranged the same way can one expect damage to occur evenly.

Future experiments with this polymer should include testing it at different thicknesses and at different potentials, trying to determine how to make it last as long as possible. Great care in producing identical films and applying as accurately as possible exactly the same voltage should increase the lifetime of the polymer, facilitating its future entrance into widespread use.

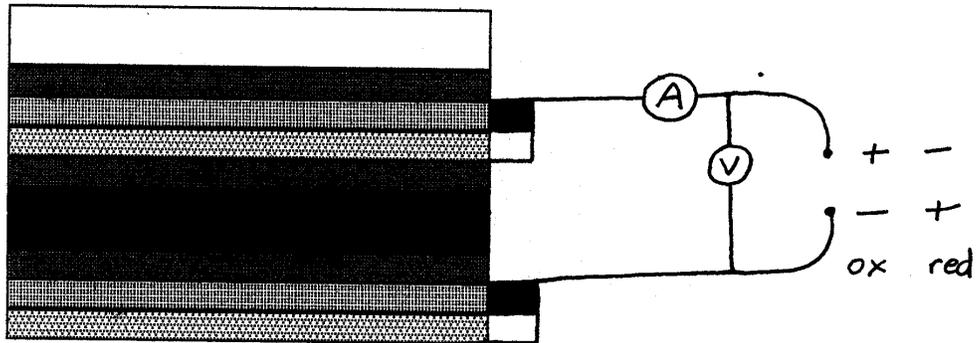
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Figure 1

Diagram of the Electrochromic Cell



Order of Layers from Top to Bottom

- ZnSe or glass window
- Electrolyte gel (ELG) layer
- PProDOT- Me₂ Film, *originally doped*
- Gold Coated, Silted Mylar Electrode
- ELG Layer
- Separator (Polypropylene)
- ELG Layer
- PProDOT- Me₂ Film, *originally neutral*
- Gold Coated, Silted Mylar Electrode

Figure 2

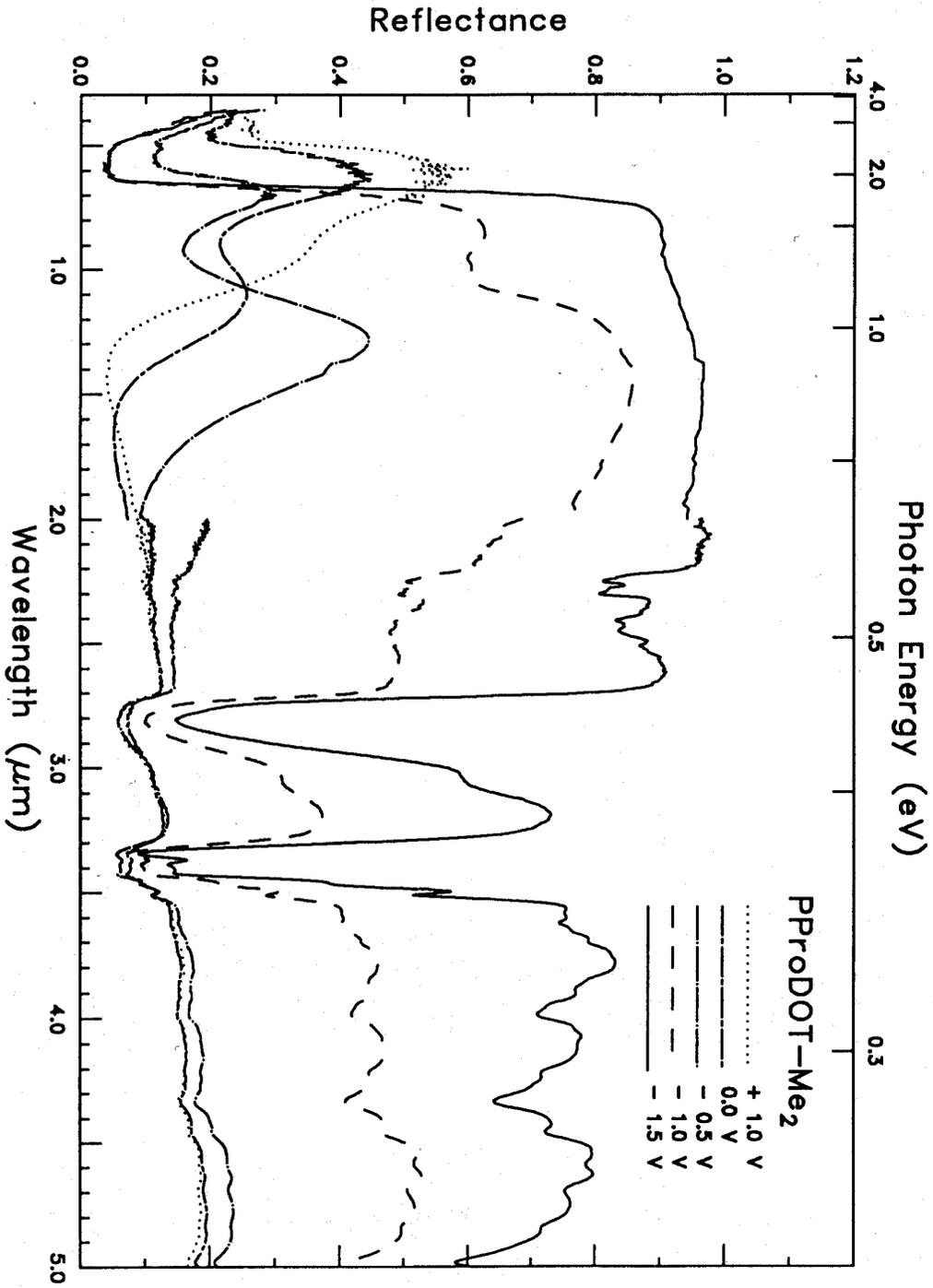
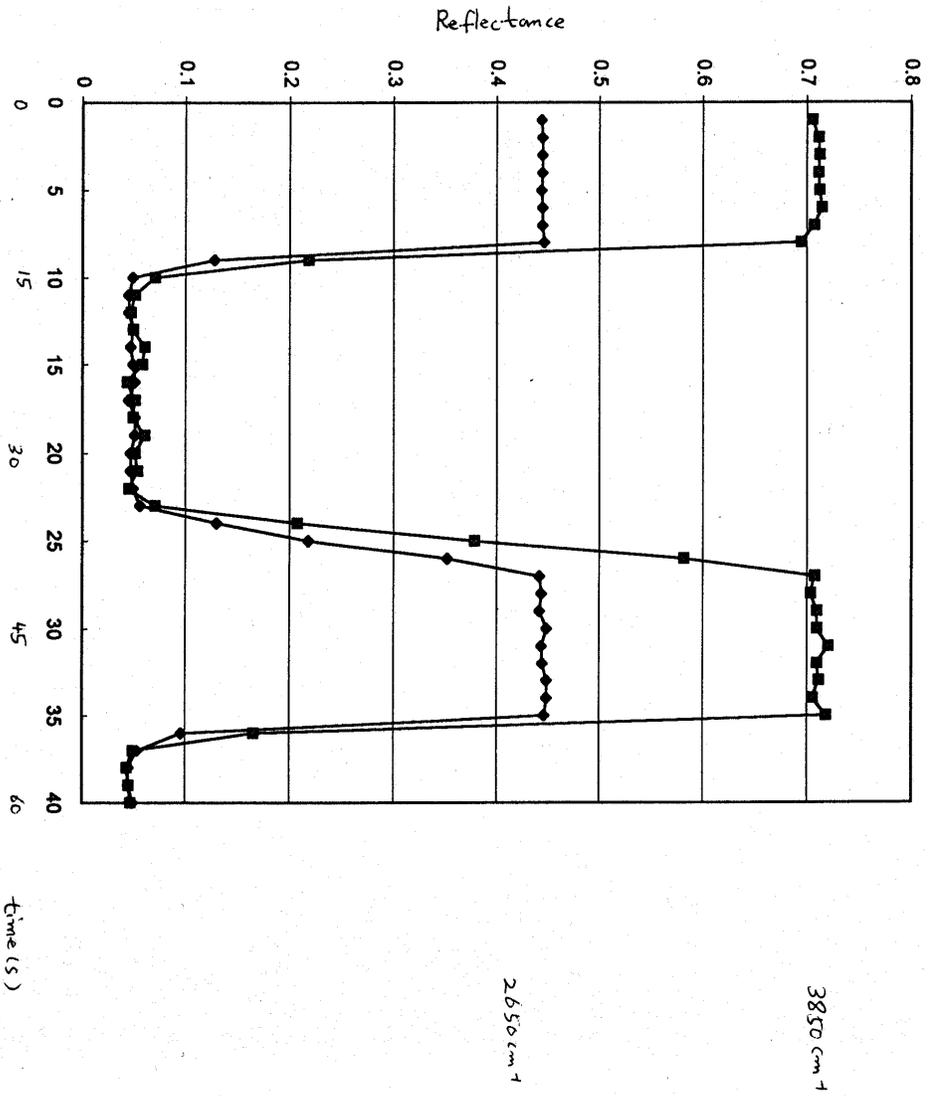


Figure 3



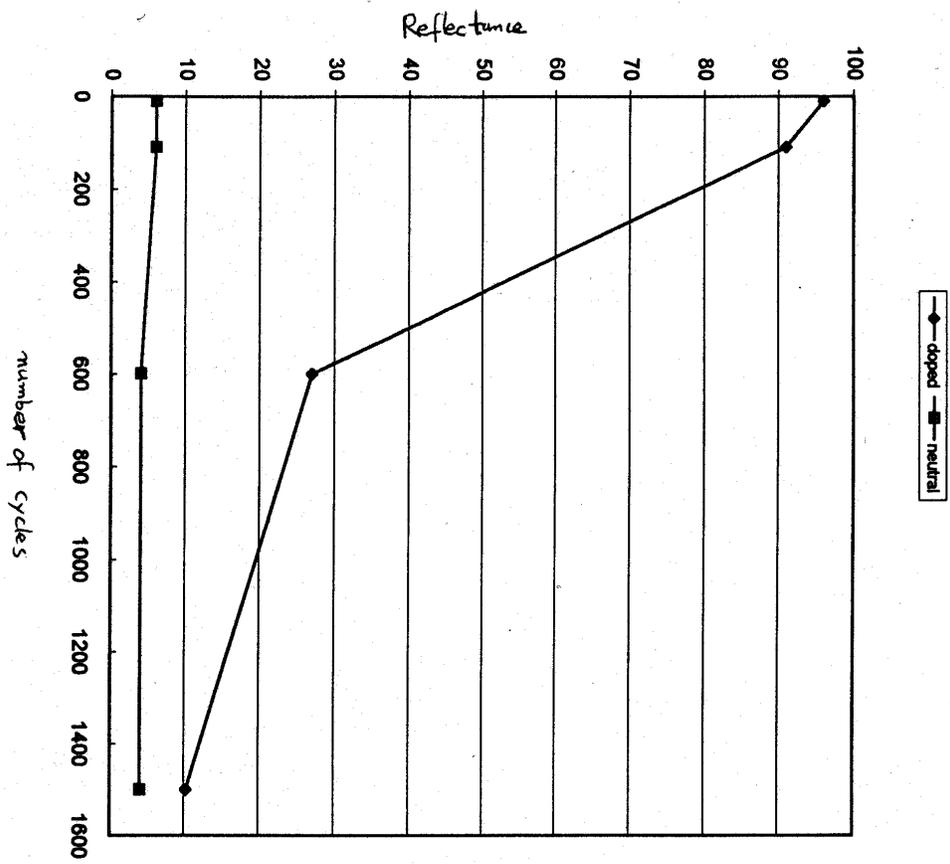


Figure 4

$$\lambda = 1350 \text{ nm}$$

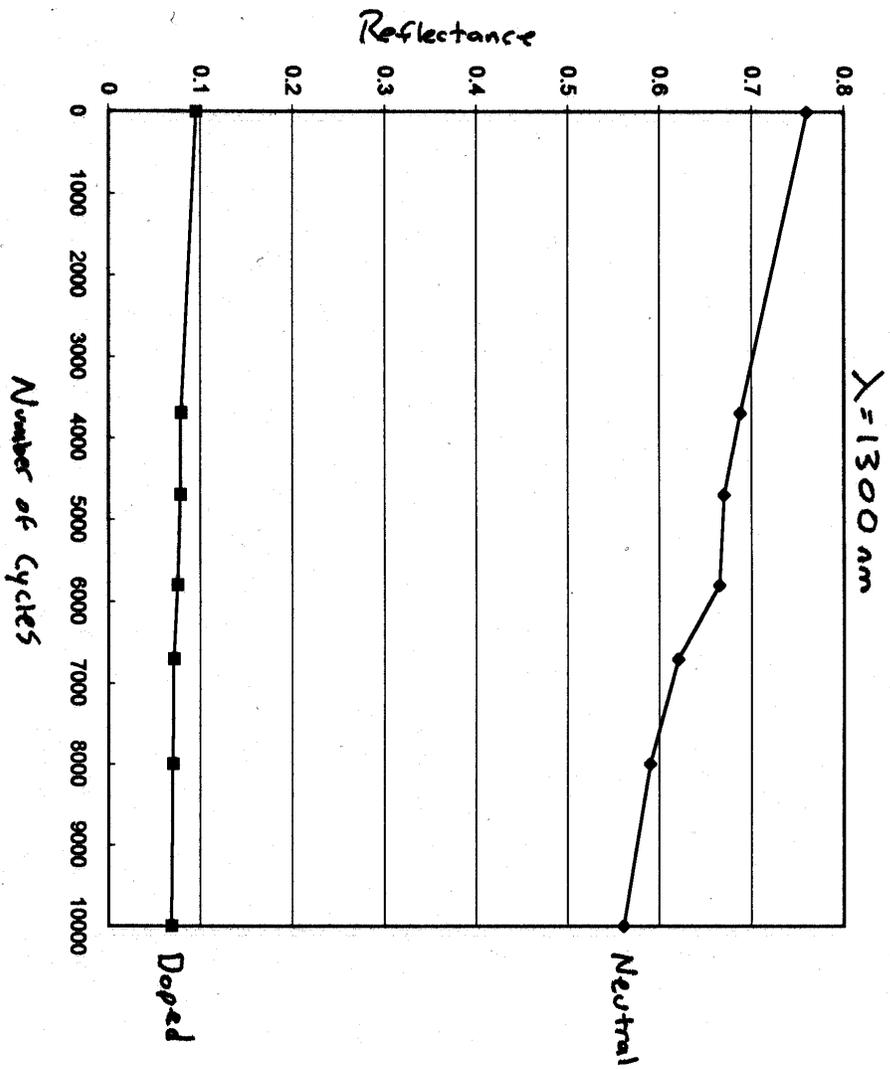


Figure 5

Fig. 6

PProDOT-Me₂

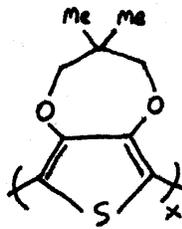


Fig. 7

Typical Conjugational Defects

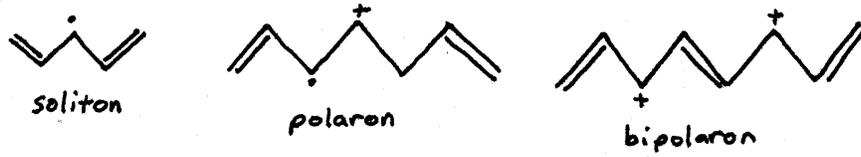
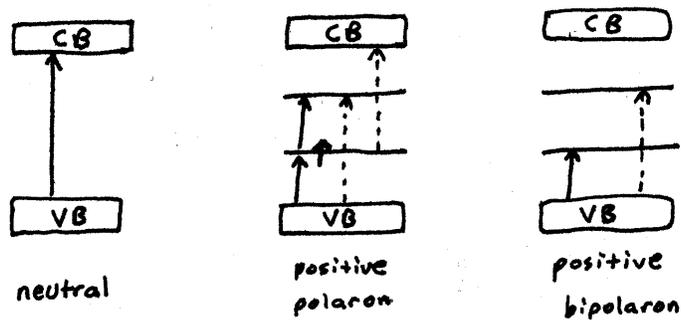


Fig. 8

Band Structure



(Taken from Ref. 5)