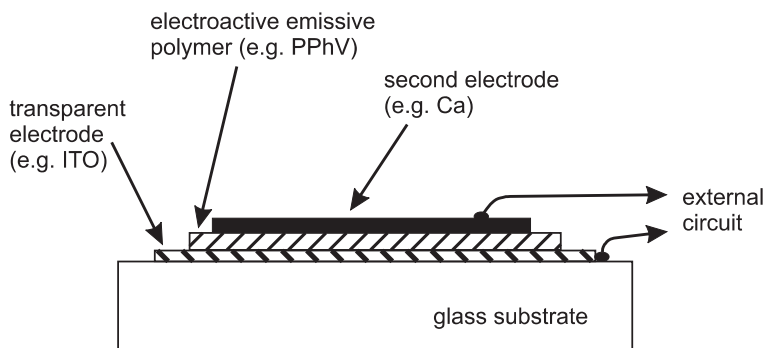


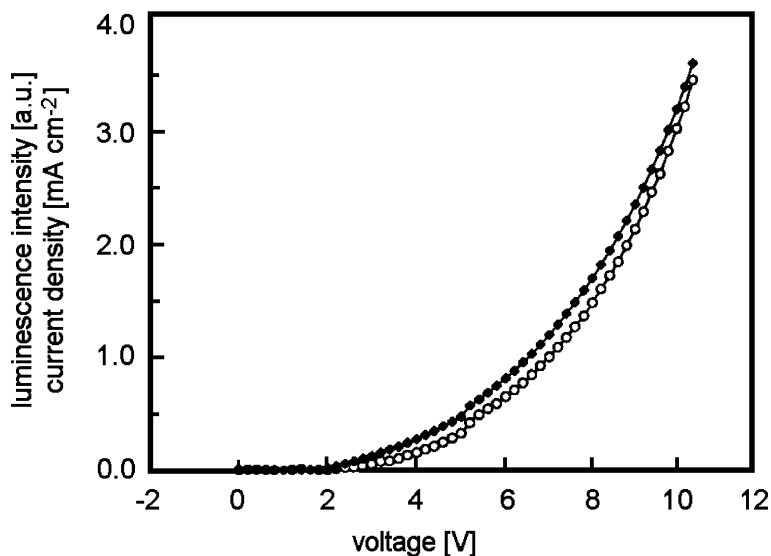
## Conjugated Polymers

The large majority of polymers, first of all the broadly used commodity materials polyethylene, polypropylene, poly(ethylene terephthalate) or polystyrene, have similar electrical and optical properties: They are insulators and they are colorless, i.e., they possess no mobile charges and the lowest electronic excitations are in the UV region. There exists a peculiar class of polymers with quite different properties; these are polymers with conjugated double bonds in the main chain. They are semiconductors or conductors and interact with light.

Figures 7.1 and 7.2 depict a characteristic observation. A thin film of poly-(phenylene vinylene) (PPhV) covered with two different electrodes made of an indium-tin oxide alloy (ITO) and calcium, respectively, is placed on a glass substrate and then connected to an external source of current. Nothing happens up to a voltage of 2 V, but then a flow of current sets in and grows with further rising voltage. Simultaneously with the onset of current the PPhV film begins to emit light, with an intensity proportional to the current. The effect is known as **electroluminescence**. A setup with such a performance is called a **light emitting diode**, abbreviated LED. The word ‘diode’ hereby



**Fig. 7.1.** Principal set-up of a polymer LED device

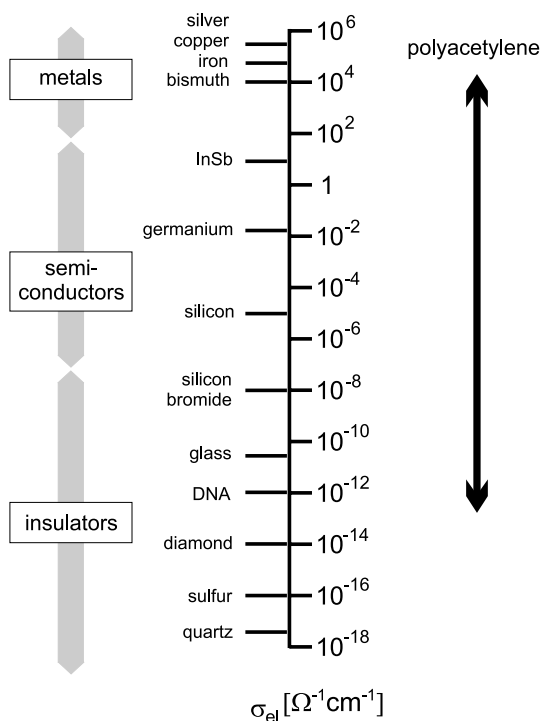


**Fig. 7.2.** ITO/PPhV/Ca LED: Variation of the current density (*filled symbols*) and the luminescence intensity (*open symbols*) with the applied voltage. From Friend and Greenham [86]

indicates that the current can flow only in one direction; if the voltage direction is reversed, practically no current flows. The active element in this **organic light emitting diode**, shortly OLED, is the **conjugated polymer** poly(phenylene vinylene). All conjugated polymers possess conjugated  $\pi$  electrons, i.e., electrons that are delocalized rather than being part of one valence bond. Excitation energies of conjugated  $\pi$  electrons are usually in the visible range and they are, therefore, addressed as being **optically active**. A selection of prominent examples has already been given in Table 1.3 in Chap. 1.

It was a second, really spectacular property that initiated the interest in conjugated polymers. In 1977 it was found by Shirakawa, Heeger and McDiarmid that films of polyacetylene (PAC) increase their conductivity tremendously when they are exposed to iodine vapor, from a basic value at the lower end of the semiconducting range up to values comparable to metals. Figure 7.3 represents these iodine dopant induced changes in a comparison with other materials. They encompass the enormous range of seventeen orders of magnitude.

It is understandable that these unusual findings triggered intense activities in research and development. The first conjugated polymers under study were all unstable in air and it was very difficult to prepare films. Suitable chemical modifications then succeeded to produce stable materials. They can be processed from solution or even the melt, sometimes via a conversion of short-chain precursors.



**Fig. 7.3.** Range of conductivities covered by doped PAc in a comparison with other materials

To provide a brief introduction into this peculiar class of polymer materials, in this chapter we first consider the elementary optical excitations, then discuss the electroluminescence, and finally deal with the conduction properties and the magnetism of doped samples.

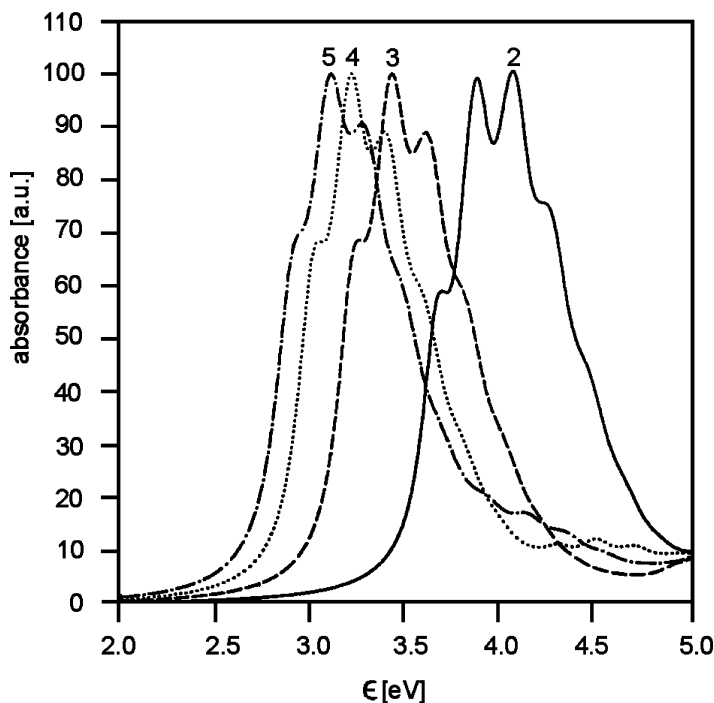
## 7.1 Electrooptic Activity

### 7.1.1 Excitons and Free Charges

Considering the physical background of the optical and electrical activity of conjugated polymers several questions immediately come up, namely:

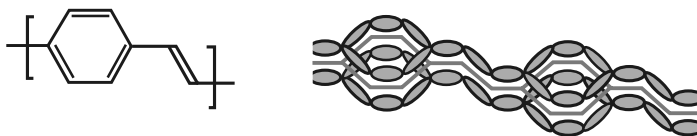
- What is the nature of the excited states that are created when photons are absorbed?
- What transitions show up in the subsequent luminescence?
- What levels are used by charge carriers when a current is flowing?

We discuss these in this section.



**Fig. 7.4.** Optical absorption spectra of two-ring, three-ring, four-ring, and five-ring oligomers of phenylene vinylene. A shift to lower energies with increasing length of the molecule is observed. From Cornil et al. [87]

Regarding the first question it is instructive to have a look at the experimental result presented in Fig. 7.4. The figure shows absorption spectra in the visible range, which were obtained for a series of oligomers of phenylene vinylene. The four presented absorption bands all have a similarly fine structure and are shifted against each other; the higher the number of monomers, the lower the frequency. A first conclusion can be drawn from the invariance of the profile of the bands. Since it is independent of the number of coupled monomers it must be a property of the monomer itself. We therefore first ask about the elementary optical excitations of a monomer. Figure 7.5 presents its chemical structure on the left-hand side and on the right-hand side a sketch of the distribution of the  $\pi$  electrons. One bond of each double bonds is set up by two  $\sigma$  electrons, the other is formed from overlapping atomic  $p_z$  orbitals oriented perpendicularly to the ( $xy$ -)plane of the planar molecular skeleton. The **conjugation**, i.e., the resonance interaction between the  $\pi$  bonds results in delocalized  $\pi$  electron states. Here, these states are occupied by the eight  $\pi$  electrons of a phenylene vinylene unit. There is a highest occupied molecular  $\pi$  orbital abbreviated **HOMO**. Above it there exists a **gap** and it extends up to next level, the lowest unoccupied molecular  $\pi$  orbital, shortly called **LUMO**.

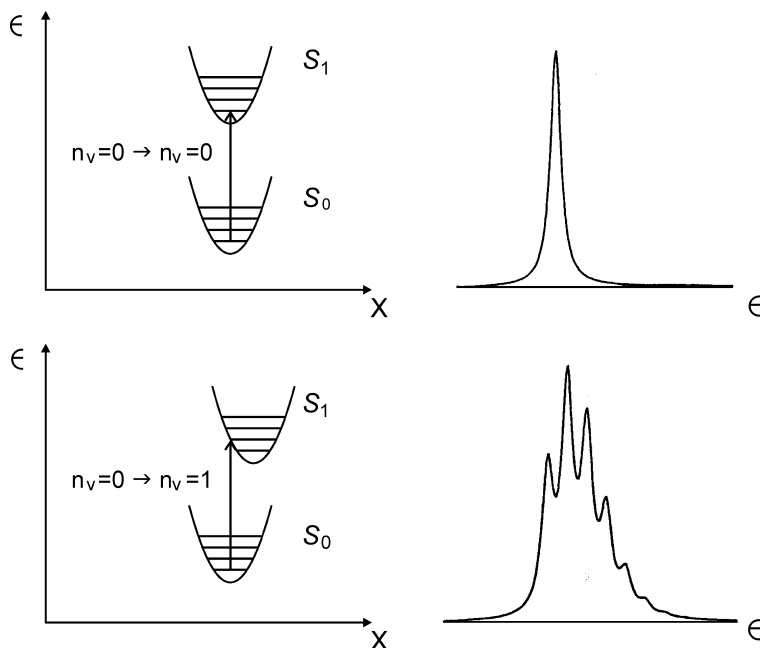


**Fig. 7.5.** (*left*) Structure unit of PPhV. (*right*) Clouds of  $\pi$  electrons in a unit, placed above and below the plane of the CC backbone. The *lines* connecting the carbon atoms represent the  $\sigma$  bonds

For conjugated polymers the gap energy is in the range of 1.5 eV to 3 eV, i.e., in the range of visible light and the near infrared, similar to anorganic semiconductors. As always in the ground state of a multielectron system with an even number of electrons, the spins compensate each other so that a singlet state, denoted  $S_0$ , results.

The absorption bands in Fig. 7.4 are to be assigned to the lowest possible one-electron excitation. This is accomplished by a transfer of the electron at the HOMO level to the next higher state. One might think at first that this is the LUMO level, but this is incorrect. The LUMO level would indeed be occupied if a ninth electron were added to the monomer. If, however, the electron in the HOMO level is excited, this level is left empty, and the then positively charged monomer exerts an attractive Coulomb force. The force reduces the excitation energy, which now falls below the gap energy. The thus formed state can be thought of as a coupled electron-hole pair and is named an **exciton**. In order to be optically active, the transition must have a non-vanishing transition dipole moment. One requirement for this is an unchanged total spin. Hence, this exciton state is necessarily a singlet state and is denoted  $S_1$ .

The fine structure of the bands follows from the fact that together with an electronic excitation also vibrations of the molecular skeleton are induced. There is a prerequisite for such a common electronic and vibrational excitation: It only happens if the transfer of the electron to a higher level leads to a change in the molecular structure, i.e., some change in bond lengths and bond angles. Figure 7.6 explains this coupling, dealing with two possible situations. The **Franck-Condon principle** states that electronic transitions are very rapid compared to motions of the nuclei setting up the molecular skeleton. Hence, they always take place at constant positions of the nuclei. In the drawings on the left-hand side of Fig. 7.6 transitions are therefore described by an arrow in the vertical direction, starting from the vibrational ground state ( $n_v = 0$ ) in the electronic ground state  $S_0$ . The variable  $X$  represents here some displacement coordinate. If the structure were not affected by the electronic excitation, the transition would automatically lead into the vibrational ground state of  $S_1$ , as indicated in the upper left figure. Then, as shown on the right, only one sharp absorption band is expected, which is rarely seen. On the other hand, if the electron transfer also produces a shift



**Fig. 7.6.** Appearance of the exciton band profile if the excitation leaves the structure of the molecule unchanged (*top right*) and if it leads to some change (*bottom right*). The *left-hand side* explains the difference of the spectra by applying the Franck-Condon principle;  $X$  represents a displacement coordinate

in the equilibrium value of the structure coordinate  $X$ , the electronic excitation is necessarily coupled to an excitation of a vibrational quantum. This is explained by the lower left figure, where the vertical arrow ends at  $n_v = 1$  in the  $S_1$  level. In this case, there also exist non-vanishing probabilities for transitions to even higher and also lower vibrational levels. As a result, a band with a fine structure appears, as shown on the right side, and exactly this is observed in the experiment.

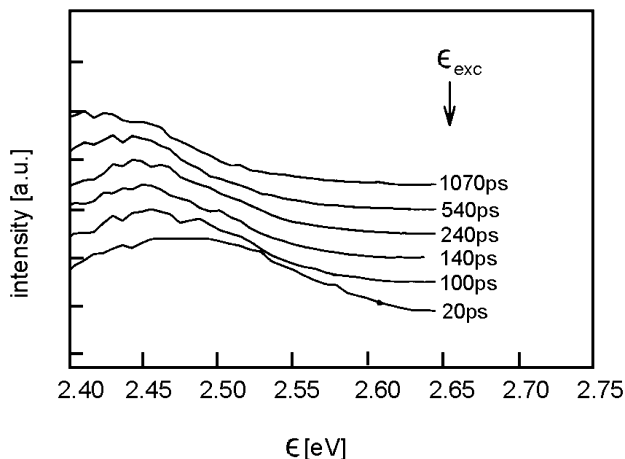
The **red shift** of the bands following from an increase of the molar mass of the oligomer is a well-known phenomenon. The continuing interaction between the  $\pi$  electrons of the coupled monomers extends the conjugation over the whole chain. The interaction further stabilizes all the  $\pi$  electrons, i.e., leads to a drop of all energy levels and a lowering of the energy difference between  $S_0$  and  $S_1$ . There is another important consequence of the interaction: If an exciton is created at some monomer by the absorption of a photon, it will not remain stationary, but propagate. After a short time it can be found on each monomer of the chain with equal probability. An exciton carries energy. To move an exciton, i.e., the energy that it represents, it is not necessary to move the constituting electron-hole pair itself. A shift of the energy can also be achieved by a simultaneous decay-excitation process in two

neighboring monomers. The rate of this transfer depends on the overlap of the associated wave functions, as is described by the **Förster mechanism**. The delocalization of the exciton that extends in the stationary state over the whole oligomer concerns both the excited electron and the created hole. The mean distance between the electron and the hole varies between different materials. For conjugated polymers it lies above the monomer diameter, typically being of the order of a few monomer lengths. Excitons are also a characteristic feature in the excitation spectra of anorganic semiconductors. There, the electron–hole distance is larger, corresponding to many lattice cells. These bound pairs are addressed as **Mott–Wannier excitons**. On the other hand, for excitons found in molecular crystals or ionic solids both the electron and the hole remain within the size of one molecule. These excitons are known as **Frenkel excitons**. The excitons in conjugated oligomers or polymers have an intermediate position, in between the Mott–Wannier and the Frenkel type.

In a perfectly ordered solid or a perfectly ordered macromolecule excitons move according to quantum-mechanical kinetics, i.e., like wave packets. Because this requires strict phase relationships in space and time, this mode of motion, addressed in the literature as **coherent motion** of excitons, is perturbed by all deviations from regularity. Chains of conjugated polymers always include various defects such as kinks and torsions. These break the conjugation. Typically, regular sequences extend only over five to ten repeat units. The results of measurements for a series of oligomers like the ones displayed in Fig. 7.4 can be used for the estimate. The red shift of the exciton frequency  $\omega$  with increasing monomer number,  $n$ , can be described by the equation

$$\omega(n) = \omega_0 + \frac{\Delta\omega}{n} . \quad (7.1)$$

Applying this to the exciton frequency observed for a polymer gives the number of conjugated structure units  $n$ . Conjugated polymers are semicrystalline systems, built up of crystalline and amorphous regions, and the crystallites often contain a high amount of defects. As a consequence, the coherent mode of motion is only found within ordered crystalline domains with sizes in the nm range. Long-range energy transfers in such a structure remain possible, but by a much slower **incoherent** kind of exciton motion, to be described as a diffusive **hopping process**. Referring to this rate determining process only, a conjugated polymer in the solid state resembles an **ensemble of domains** of varying size, from ordered assemblies of regular chain sequences down to single monomers incorporated in the coiled chain parts in the amorphous regions. With the size of these sites the excitation energy also varies, the minimum being found for the largest domains. Even under these conditions of a varying excitation energy, excitons can carry out hopping motions between adjacent domains. The highest transfer rates are found for **resonance transitions** between domains with equal excitation energies, but a transition to a domain with a lower or higher energy is also possible, although with a lower rate. The latter moves must be supported by the creation or annihilation of phonons.



**Fig. 7.7.** PPhV: Time-dependent change of the fluorescence spectrum after an excitation pulse at 2.65 eV (arrow). The waiting times are given. From Bässler [88]

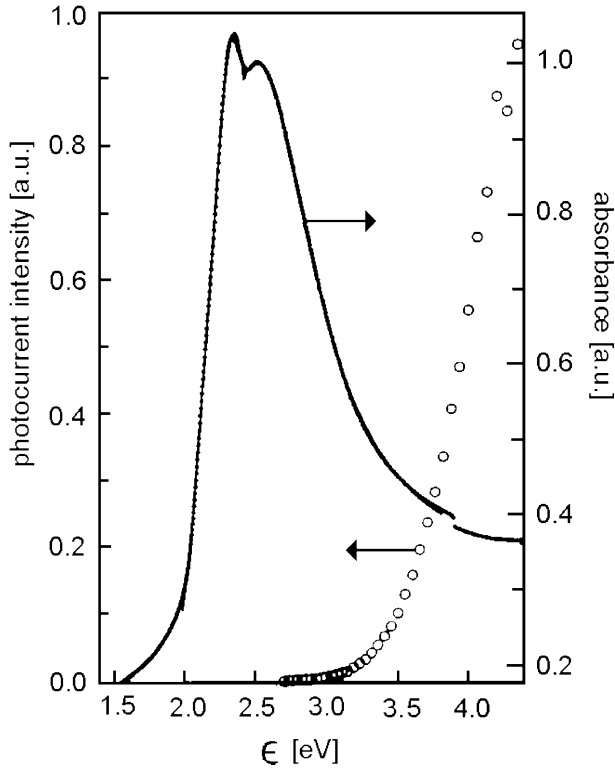
Of course, the time an exciton can use for a motion is limited. At any time an exciton can spontaneously annihilate under the emission of a photon, thus contributing to the luminescence. In addition, there always exist mechanisms of a non-radiative decay. Figure 7.7 shows an experiment that reflects the diffusive motion of excitons within the **energy landscape** associated with the broad **density of states** distribution provided by the ensemble of domains. The figure shows luminescence spectra observed subsequent to a short pulse after a certain waiting time. One finds a time-dependent change of the luminescence spectrum with a shift to lower energy with increasing time. Hence, there is a tendency of the excitons to diffuse to the domains with lower excitation or decay energy. The process can be modeled and the development of the luminescence reproduced.

Due to the coupling of the excited electron to the hole left back on the HOMO level, excitons are non-charged particles that cannot contribute to an electrical current. A current requests the motion of free charges, either electrons or holes. These can indeed exist in conjugated polymers. They are found if

- an exciton dissociates into a free electron and a free hole after an additional energy input,
- rather than creating an exciton, an absorbed photon immediately produces a free electron–free hole pair,
- free holes or electrons are supplied by dopants or injected from the electrodes.

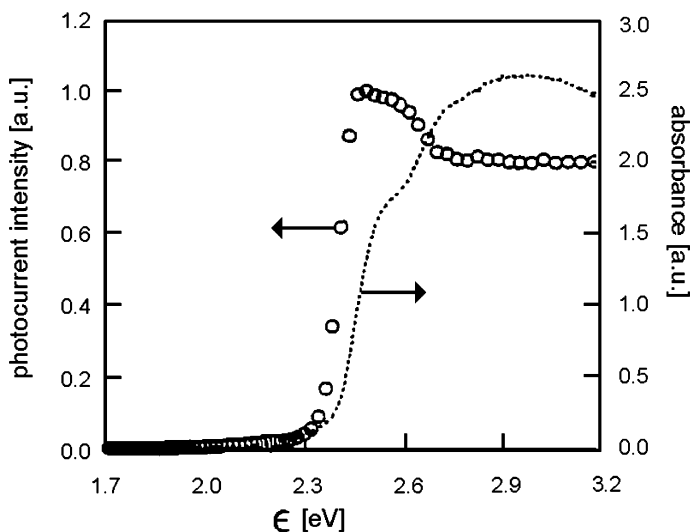
The experiments shown in Figs. 7.8 and 7.9 provide examples for the first two processes.





**Fig. 7.8.** PdAc: Photoconductive spectral response (*circles*) compared to the optical absorption spectrum (*continuous line*). From Pakbaz et al. [89]

The first figure presents the **spectro-photoconductive response** of poly(diacetylene) (PdAc). Some low voltage is applied to the sample, but at first virtually no current is observed. The sample is then illuminated by monochromatic radiation under variation of the frequency. When coming from low frequencies the photon energy of 3 eV is reached, a flow of current sets in and rises with further increasing photon energy. Obviously, if photons with energies above this limit are absorbed they create free carriers in the sample, thus enabling a current to flow under the applied voltage. Interesting is the comparison with the frequency dependence of the absorbance, which is also shown in the figure. Photon absorption begins much earlier, already at 1.5 eV, but is at first not associated with a photocurrent. Hence, in this first frequency range only excitons are created. The energy difference between the peak at 2.4 eV associated with the creation of an exciton and the onset of the photocurrent amounts to about 0.6 eV. Its meaning is clear: It represents the dissociation energy of the exciton, i.e., the electron-hole binding energy.

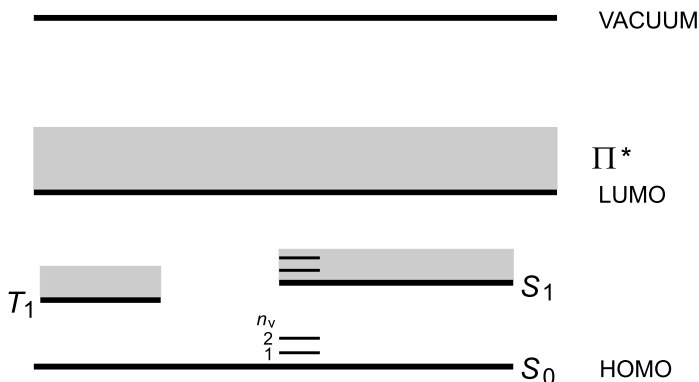


**Fig. 7.9.** PPhV: Photoconductive spectral response (*circles*) compared to the optical absorption spectrum (*continuous line*). From Lee et al. [90]

The second example, which deals with poly(phenylene vinylene), shows that this difference can also be very small and virtually vanish. Here, the onset of the absorption is practically identical with the onset of the photocurrent. The reason for this peculiar property of poly(phenylene vinylene) is still under discussion. There might exist sites (in particular places located at the film-electrode interface) where the additional energy necessary to dissociate the exciton is spontaneously provided.

As has been mentioned, transferring an electron up to a higher level in general leads to changes in the structure of the molecular skeleton. A structural response is also to be expected for a freely moving electron or hole: It polarizes its surroundings on the chain. This polarization generally leads to an energy decrease. Theoretical estimates for this drop yield a value of the order 0.1 eV and indicate an extension of the polarization over a couple of monomers. The polarization remains localized and moves together with the electron or hole. Many treatments in the literature emphasize this effect, then dealing with negatively or positively charged moving particles named **polarons** instead of just considering the motion of free electrons and holes.

Like excitons, electrons, holes or polarons also carry out a hopping motion between the domains in a conjugated polymer. Each domain provides unoccupied states around the LUMO and HOMO level for electrons and holes, respectively. They are delocalized within the domains and vary, as for the excitons, in their energy with the domain size. The tails of the corresponding density of states distributions act as shallow traps that keep the charges temporarily fixed.

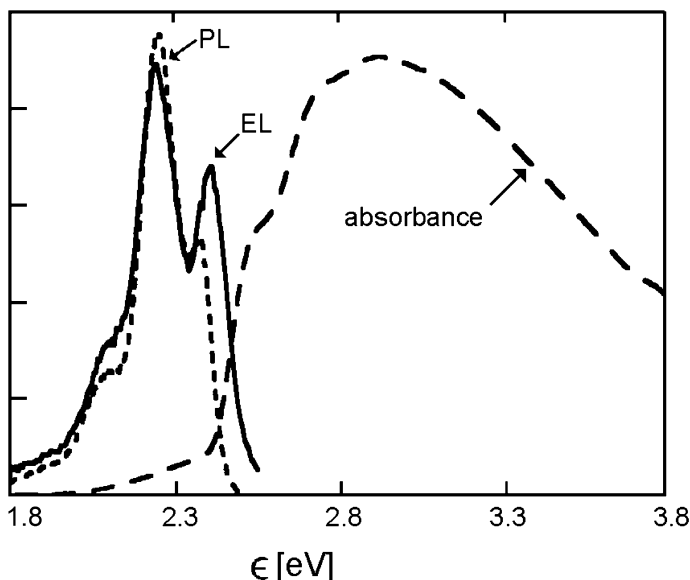


**Fig. 7.10.** One-electron levels and multielectron states created by excitations of one  $\pi$  electron in an ordered domain of a conjugated polymer. Prior to the excitation, in the ground state  $S_0$  the electron occupies the HOMO level.  $S_1$  denotes a first order singlet exciton with an energy at the lower bound of the associated vibronic band. The creation of an exciton is in general coupled to simultaneous vibrational excitations;  $n_v$  are vibrational quantum numbers.  $T_1$  denotes a first order triplet exciton at the lower bound of an associated vibronic band. The LUMO level is at the lower edge of the band  $\Pi^*$  of states with one non-bonded electron. The VACUUM level is that of electrons with vanishing kinetic energy outside the sample

Figure 7.10 summarizes once again the energetic situation, giving a scheme for the energies of all the discussed states, both one electron levels and multielectron states, referring to one domain. One additional feature is included. On the left-hand side a further multielectron state denoted  $T_1$  is shown. It represents a first order **triplet exciton**. It differs from the singlet exciton in the total spin, which here has the quantum number 1. It is not possible to create triplet excitons by a photon absorption starting from the ground state  $S_0$  since it necessitates a change in the spin direction. However, there exists another pathway for the formation of triplet excitons, namely a spontaneous coupling of a free electron and a free hole; they may have been created by an injection from the electrodes or the dissociation of singlet excitons. Spontaneous decays of triplet excitons under the omission of photons are forbidden, strictly speaking, they still remain possible but occur with an extremely low rate. Triplet excitons decrease the efficiency of light emitting diodes, as will be discussed in the next section.

### 7.1.2 Electroluminescence

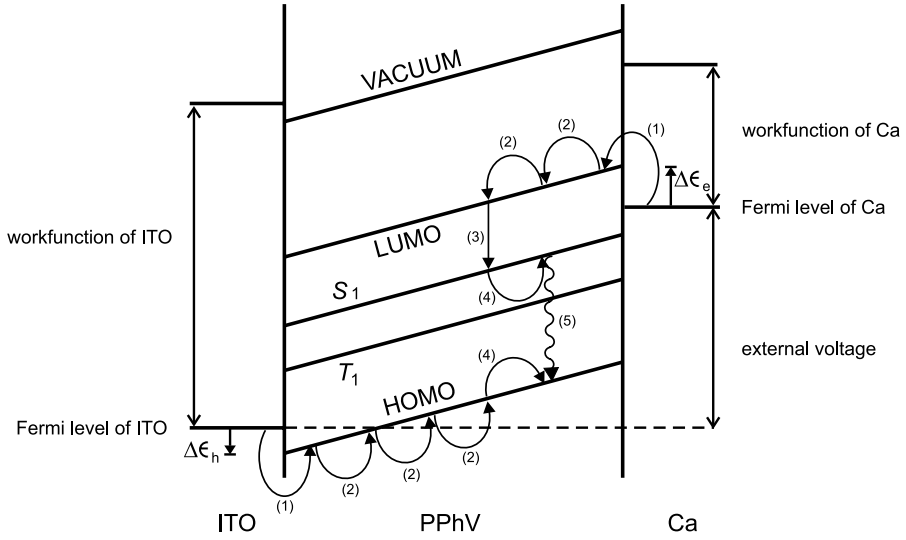
In the introduction to this chapter a light-emitting diode was described as being set up of a polymer film (PPhV) and two different electrodes (ITO and Ca) on the surfaces (Fig. 7.1). Figure 7.2 then showed that for voltages above a critical value a current coupled to the emission of light flows. Figure 7.11 now displays the spectrum of the emitted light as well. The curve denoted EL



**Fig. 7.11.** PPhV: Luminescence spectra after an electrical (EL) and a photonic (PL) excitation, shown together with the optical absorption spectrum. From Friend and Greenham [91]

represents this spectrum with a broad band with fine structure. The band is to be assigned to the vibronically broadened annihilation of an exciton. Also included in the figure is the photo luminescence spectrum (PL) observed after an excitation of poly(phenylene vinylene) by photons with energies above 2.6 eV. The two emission bands EL and PL are practically identical. Hence, both an electrical or optical excitation create the same excitons, which then annihilate under the emission of photons. The figure also shows the optical absorbance spectrum of poly(phenylene vinylene). It sets in at the frequency of the exciton and shows a strong rise at 2.4 eV. Here the photon energy reaches the value that is required to excite one electron from the HOMO to the LUMO level, i.e., to create a free electron and a free hole.

A discussion of the functioning of a polymer LED can be based on the energy level scheme given in Fig. 7.12. It deals with the conditions in an LED onto which an external voltage is applied. Polymer LEDs are set up using two different electrodes. One of them, in the ITO example, has a high work function (as given by the energy that has to be supplied to transfer an electron from the Fermi level to the vacuum level). The second one, here calcium, has a low work function. When the electrodes are attached to the polymer film, **electrical double layers** spontaneously form at the interfaces; as always happens when two different conductive materials are brought in contact with each other. The layer on the metal side is very thin, the oppositely charged depletion layer near the surface of the polymer film has some extension. As a consequence, steps



**Fig. 7.12.** Energy level diagram for a ITO/PPhV/Ca LED under a voltage as given by the difference between the anode and cathode potential. Work functions of the two electrodes. Barriers to the injection of electrons,  $\Delta\epsilon_e$ , and holes,  $\Delta\epsilon_h$

in the electrostatic potential  $V$  arise at both metal–polymer interfaces. The step heights have such values that in the initial equilibrium state, i.e., the state established before the application of an external voltage, the chemical potential of the electrons, which now includes also an electrostatic contribution  $(-e)V$ , becomes identical in all three materials. Applying an external voltage leads to deviations from the current-free equilibrium state, and a current starts to flow. Within the polymer film the electrostatic potential decays. The decay of the potential that determines the electrical field,

$$E = -\frac{dV}{dx} , \quad (7.2)$$

and the current density  $j$  are related by

$$j = \sigma_{\text{el}} E . \quad (7.3)$$

$\sigma_{\text{el}}$  denotes the **electric conductivity**. For all semiconductors  $\sigma_{\text{el}}$  is to be described by

$$\sigma_{\text{el}} = e c_e \nu_{\text{el},e} + e c_h \nu_{\text{el},h} . \quad (7.4)$$

$c_e$  or  $c_h$  denote the number densities of electrons and holes. The variables  $\nu_{\text{el}}$  represent **electric mobilities**. They give the ratio between the mean velocity  $\bar{u}$  of a charged particle and the acting electric field

$$\nu_{\text{el}} = \frac{|\bar{u}|}{E} . \quad (7.5)$$

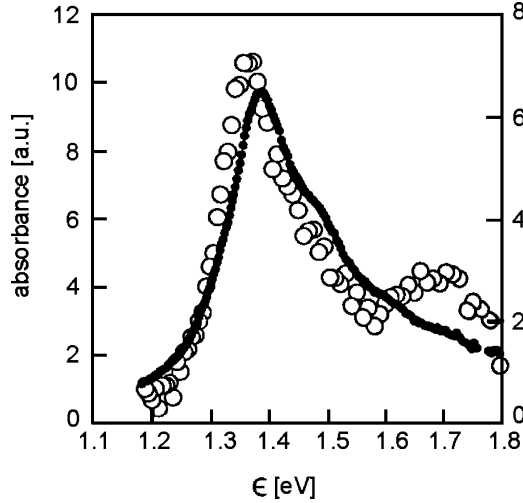
Compared to anorganic semiconductors electric mobilities in conjugated polymers are generally low.

If an LED is activated by an external voltage, from the cathode electrons change into the polymer film to the LUMO level of mobile free electrons and holes are simultaneously ejected by the anode and enter the HOMO levels. The barriers to be surmounted have heights  $\Delta\epsilon_h$  and  $\Delta\epsilon_e$  and the entrance steps are represented by the curved arrows denoted (1). As is obvious, under the given conditions with electrodes with strongly differing work functions, cathode and anode cannot be exchanged. The then arising high barriers allow for only a low current. The setup thus indeed has rectification properties, i.e., is a diode. Within the polymer layer both the electrons and the holes move by a hopping process from domain to domain, directed by the applied field as indicated by curved arrows (2). Sometimes it happens that an electron and a hole arrive at one site at the same time. Then an exciton can form under a transfer of the binding energy to the lattice (3). The exciton also carries out a diffusive motion between the domains (4). However, being a neutral particle, its hopping motion is random, i.e., non-directed. At some time the exciton will spontaneously annihilate under the emission of a photon (5).

Poly(phenylene vinylene) and also other conjugated polymers have an imbalance in the properties of electrons and holes. The entrance barrier is higher and the mobility is lower for the electrons, and as a result electrons are accumulated near the cathode. As a consequence, the emission region also shifts to the neighborhood of the cathode. Near a metal surface excitons annihilate more frequently in radiationless manner and the luminescence efficiency drops. To avoid this undesired effect modern LEDs are often constructed from two organic layers, one preferentially transporting electrons (ETL), and the other one, the conjugated polymer, transporting holes (HTL) first of all. For such an ITO-HTL-ETL-Ca LED the light emission region moves toward the HTL-ETL interface in the center and the rate of radiationless decays decreases.

If an electron and hole couple within one domain, either a singlet ( $S_1$ ) or a triplet exciton ( $T_1$ ) forms. Since triplet excitons have three independent states, corresponding to quantum numbers  $S_z = 1, 0, -1$  for the spin component in the  $z$ -direction, while only one state exists for the singlet exciton, triplets form with a three times higher rate than singlets. Their existence in a LED can be observed by spectroscopical means. Triplets possess a characteristic absorption band that relates to a transition from  $T_1$  to a higher order triplet state. Figure 7.13 shows this characteristic band for poly(phenylene vinylene). The experiment demonstrates that triplets are generally created when free electrons and holes are present; they may have been produced by either applying a current or an optical excitation with photons of sufficiently high energy.

As has already been mentioned, the existence of the triplet excitons is a disadvantage of polymer LEDs. They do not contribute to the luminescence



**Fig. 7.13.** PPhV: Absorption spectrum assigned to triplet excitons demonstrating their presence after an electrical (*open circles*) or optical (*filled symbols*) excitation. Measurements were carried out at 20 K. From Brown et al. [92]

signal of the device and, therefore, reduce its efficiency. Putting all relevant factors together, the electroluminescence efficiency,  $\gamma_{\text{EL}}$ , of a polymer LED can be described as

$$\gamma_{\text{EL}} = \phi_{\text{opt}} p_{\text{ex}} \phi_{\text{S}} p_{\text{pl}}. \quad (7.6)$$

$p_{\text{ex}}$  gives the probability that an electron and a hole entering the organic layers from the external current form an exciton,  $\phi_{\text{S}}$  describes the fraction of singlet excitons and  $p_{\text{pl}}$  denotes the photoluminescent quantum yield.  $p_{\text{pl}}$  differs from unity due to the presence of **quenching sites** offering non-radioactive decay paths to the excitons. A polymer LED represents a multilayer structure whose optical properties are affected by reflections, refraction and interference phenomena. This is globally expressed by the fourth factor,  $\phi_{\text{opt}}$ , dealing with the outcoupling, i.e., giving the fraction of photons emitted from the front surface.

The color of the light emitted by a polymer LED, which is determined by the exciton energy, can be varied by chemical substitutions or by changes in the conjugation length. The conjugation range can be reduced in controlled manner by the introduction of co-units into the chain. Another means is a dissolution of chains of the conjugated polymer in a matrix of a common polymer; Fig. 7.14 gives such an example. A ladder polyphenylene (PPh) was blended with polystyrene (PS). For a concentration of 30% of the conjugated polymer the emission line shows a broad spectral distribution (a). The distribution becomes sharper when decreasing the concentration. In the dilute limit of 1% of ladder polyphenylene one observes a line with a sharp maximum in the blue range (c).

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