Electrical Characterization of Organic Electronic Materials and Devices

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Contents

Preface

This book is the summary of more than a decade of investigation of organic electronic materials and devices carried out at the Optoelectronics Laboratory at the University of The Algarve. It is in no way a summary of the literature, though an extensive selection of references is included. (It should be made clear from the beginning that by mentioning a paper in the literature does not imply that I approve of its contents, agree with its conclusions, or even recommend its reading, nor that I fully understood its message; it only serves the purpose of mentioning works on the subject and gives a possible starting point for interested readers. Some of the papers, especially in the introductory parts, I have to admit, I did not even read thoroughly myself; the list of citations at the end is thus a mixture of references and bibliography.)

Every time a concept of electrical behavior came up, I tried to understand it by making calculations, or, more often, by making simulations, until the behavior was in-line with how I understood things to work. Often my understanding of things was wrong and it had to be changed to be in-line with simulation and results in our laboratory and results presented in the literature. Even while writing this book, I changed my thinking substantially in some places, showing that the learning curve is infinite. It also shows that, probably, this book is still full of errors and misconceptions. It is to be considered, still, an unfinished work. It should therefore not be seen as an absolute book, believing everything without questioning. It should rather be seen as a work to stimulate thinking and to help the scientist on the way with proper tools.

I also suffer from the constant need to not only understand things, but to also make the description as simple as possible, to strip away all the unneeded embellishments, and to reduce it to its important core. While obviously missing out on some descriptive power of the ideas, the gain of hopefully making it possible for many more people to understand compensates enough. In my opinion, it is not the task of a scientist to understand nature, it is rather to model it and explain it to others so that they can understand it and further build on it. If not, all gained knowledge will be lost at the end of the career of the scientist.

Never, in any case, did I assume things to be correct in the literature and just conveniently reference them away when encountering similar behavior in our materials and devices. A multitude of papers exist that are far beyond my grasp. After some failed attempts, I ignored these papers (some of them are still mentioned in this book, so that you can take a look yourself). The most remarkable result of this approach is probably the description, from the origin, of the thin-film transistor with, as final end-product, a predicted and implemented transistor based on a metal as the active layer. Looking back at it, I now consider it something completely trivial and expected. Most people will probably agree that it is trivial. However, the same reasoning also led to the accurate description of the contact effects, something that conflicts with a large number of papers in the literature.

It always gave me immense pleasure to work on the subject and to realize that, after all, nature is a fascinating complex world, but when persisting, even for a humble and ignorant human being, it is possible to understand some things. Then, the beauty lies in its simplicity. As a single starting point, I used the idea 'Think as an electron'; when thinking as an electron, the rest will follow. In case of doubt it is best to ask 'What would *I* do if I were an electron?' This is funny, in a way, but in many cases very helpful.

This work, of course, would not have come about without the help of other people. Most important in this respect is Henrique Gomes, my colleague at the Optoelectronics Laboratory. Sometimes, by just saying a couple of phrases, he pointed the way to a better understanding of things, things that would sometimes take me months or even years to figure out in all their myriad implications. Likewise, the comments and observation of Martin Taylor have been extremely helpful. The discussions with Adriano Benvenho were always a good inspiration for a lot of the work. I also thank him for proofreading this book. My students Nelson Pimenta and José Almada are thanked for implementing the transistor admittance spectroscopy system described in Chapter 6.

I hope this text is helpful to you, the reader, too. After all, that is the aim of this work.

Peter Stallinga
Faro, Portugal
February 2009

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General Concepts

1.1 INTRODUCTION

This book describes the electronic measurements of materials and devices based on amorphous materials, with an emphasis on organic electronic materials. The distinction of what is exactly an organic material is rather vague, but generally speaking it is all those materials that contain carbon. This area is rather vast (see for instance the book on organic chemistry by Wade [1]). For this work the ones that are important are those that are electrically active, basically organic semiconductors. That organic materials can be semiconductors is nothing new. Wallace has shown already in 1947 that graphite is a semiconductor [2]. (Curiously enough, graphene, a monolayer of graphite, is again a hot-topic material [3].) Recently, though, a new wave of research in organic electronics has got under way, powered by the need for cheap electronic devices or other devices that cannot be made by conventional, 'classic' semiconductors and helped by the accidental discovery that organic materials can be as conductive as metals and further stimulated by the continuing advances in technology of fabrication of materials and devices.

Two decades and a Nobel Prize after the start of this new wave of organic electronic research, commercial devices are a reality [4]; manufacturers advertise that their products have light emitting diodes based on organic materials (OLEDs), to name but an example. Like in most technological advances, the understanding of the devices lags behind. There are many issues yet to be solved. The most important may be

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the electronic processes governing the conduction of charge. On the one hand there exists the idea that the conduction consists of hopping from one molecular orbit to the other. Such hopping models centered around the molecular aspects obviously find many followers among chemists. Conduction is then considered a perturbation to the system. On the other hand there exists the solid-state-physicists approach of treating the materials like any semiconducting material and describing the electronic states of the material in the classical conduction and valence bands. The molecular properties are then treated as a perturbation. The answer will lie probably somewhere in between. However, electronic devices can only be made from semiconductor (conducting) materials. In view of this it is most obvious that existing working devices are best described by classic semiconductor theory, at least as a starting point, and changes should only be introduced into the theory when needed. However, organic electronic materials research evolved from chemistry and the publications by chemists far outnumber the publications of semiconductor physicists. Many papers describe the problems encountered when fabricating the materials, whereas the electronic parameters, such as band gap, effective mass, or electron affinity are difficult to encounter. The electrical characteristics of the resulting materials often serve as a by-product of the chemical research, without even trying to understand or describe them well. As an example, often the mobility is presented as a parameter to describe the quality, the 'success', of the new proposed production route, or to compare one material with another [5]. Review articles often present tables with best mobilities, for instance to show the evolution over time [6–8]. However, just presenting the mobility value without specifying the conditions is as meaningless as presenting a current without specifying the applied bias. In view of this, it is often difficult to compare the results presented by different research institutes. The current book is an attempt to explain the mechanisms involved in the electrical characteristics of organic materials and the measurement techniques used to determine the relevant parameters. The starting point is the theory of the 'old school' of semiconductor devices which is very well described by the classical book of Sze [9], a book which will be cited many times throughout this work. The reader is advised to obtain a copy of this book. More recent books include novel devices, such as thin-film transistors (TFTs), for example the book by Shur [10]. There also exist good books about the measurement techniques in general. The book by Blood and Orton may serve as an example [11]. The current work describes how and when the ideas of these books, written for classical semiconductors, can be applied to organic materials and when they need to be changed or adjusted before application.

As a first observation, a significant difference can be pointed out between classical and organic semiconductors. In classical semiconductors, namely silicon, germanium and GaAs, with the exception of diamond, the band gap, the distance between the conduction band and the valence band, is rather small, in the order of 1 eV, see Table 1.1. In most organic semiconductors, this band gap is much larger and is in the order of 2–3 eV. As a direct result, the optical processes have a larger range and blue photovoltaic devices are feasible. However, the large band gap also allows for the existence of deep levels. These deep levels can make the electronic processes very slow. To give an example, the 'lifetime killer' impurity of gold in silicon introduces a near midgap level with a depth of approximately 0.6 eV. This midgap level of gold in

Table 1.1 (a) Physical properties of some classical semiconductors. (b) Band gaps of some organic semiconductors

(a)

Property	Si	GaAs	C
Atoms/molecules (cm^{-3})	5.0×10^{22}	4.42×10^{22}	1.8×10^{23}
N_C (cm^{-3})	2.8×10^{19}	4.7×10^{17}	10^{20}
N_V (cm^{-3})	1.04×10^{19}	7.0×10^{18}	10^{19}
ε_r	11.9	13.1	5.7
Electrons m^*/m_e	0.26	0.067	0.2
Holes m^*/m_e	0.16	0.082	0.25
Electron mobility ($\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$)	1500	8500	4500
Hole mobility ($\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$)	450	400	3800
Energy gap (eV)	1.12	1.424	5.47
Electron affinity (V)	4.05	4.07	

(b)

Material	Band gap (eV)
PEDNT	0.95
PEDOT	1.6
Polythiophene	2.1
PPV	2.4
PPP	3.0
Polypyrrole	3.2
Pentacene	1.82
Tetracene	3
Sexithiophene (T6)	2.87
Alq_3	2.7

silicon, the fastest possible electron–hole recombination path in silicon, has a recombination time in the order of microseconds. The lifetime of thermal excitation from a level is exponentially dependent on the ratio of level depth and average thermal energy ($kT = 26\,\text{meV}$ at room temperature) [9]. Thus, a typical organic wide band gap material, with a band gap of 2.5 eV has a midgap level that is about 0.6 eV deeper. This translates to a factor $\exp(600/26) = 10^{10}$ in the time constant when assuming the prefactor in the capture cross-section to be constant. In other words, a midgap trap in silicon has a relaxation time in the order of microseconds, whereas in an organic material it causes transients in the order of tens of kiloseconds. Other levels suffer from this effect as well, albeit to a lesser extent. Since many impurity levels derive their electronic structure from the band states, a widening of the band gap might cause a deepening of the impurity levels. This makes organic materials notoriously slow. Ring oscillators have been fabricated working only in the kHz range, where for silicon they can easily be made operating at GHz frequencies. However, the application of organic materials lies not in the area of fast electronics but rather in the area of cheap electronics, large-area electronics [6], or electronic devices that cannot be made or are difficult to make by classical materials. One has to think here about things like printable [12–17], ink-jet printable [18, 19], and flexible electronics [15, 20–23] or electronic textiles [24]. In this respect fully organic devices stable in air are interesting [25]. Further, imagine a display on curved surfaces, etc. Or the color-switchable light emitting device [26]. The ultimate goal is to reach the single-molecule electronics level [27]. With this goal in mind, a wave of research was focused on nanoscale technologies, such as incorporating carbon nanotubes [28, 29] or nanowires [30].

Since, in contrast to inorganic materials, the number of organics is sheer infinite, an organic material can be synthesized that meets any need, for instance, for sensors [31–36]. Immediately it was obvious that organic materials are highly compatible with biological materials and are thus ideal partners in bioelectronics, including biodetectors (transducers) [37–39] or signal processing in biomolecular electronics [40, 41]. DNA or its constituent nucleic acids themselves can easily serve as the active material in (thin-film) transistors [41–43]. Interestingly, in these cases the behavior of the devices is adequately described by the ideas presented here.

Another fundamental difference is the difficulty of making organic materials with the same level of purity and crystallinity as, for instance, silicon. As discussed by Caserta *et al.*, the treatment of the material by a band model might seem inadequate for such noncrystalline materials. However, as stated by them by referring to papers of Ioffe and Regel and Gubanov, ‘a periodic electric field of the lattice is not essential for the occurrence of typical semiconducting properties and the band model may be applied also in the case in which there is a loss of periodicity of the lattice’ [44]. Long-range order is not needed to give the material semiconducting properties. The edges of the bands are not well defined, though. In other words, noncrystalline (disordered) materials can be treated by semiconductor (band) theory with nondiscrete bands.

Together with the noncrystallinity comes a large density of trap states and they severely change the electronic behavior, as will be shown throughout this book. Trap states are deep localized states that can capture carriers that would otherwise contribute to conduction. It is irrelevant if the trap states originate from the disorder of the material or from impurities. Once captured by a trap, these charges are unavailable for conduction (in other words, the mobility is zero). There exists also models to include hopping or tunneling conduction via traps [45]. These models do not need any band states and are therefore more closely related to insulating materials than semiconducting materials. As a rule of thumb, it can be said that when the (intrinsic) mobility is below $10^{-4}\,\text{cm}^2\,\text{V}^{-1}\text{s}^{-1}$ the conduction is most likely to be of hopping type and above this limit it is more likely to be of band type. The reason for this is that if conduction is large, the time spent on an individual site is short, and this causes a wide band because of Heisenberg’s Uncertainty Relation [46], $\Delta t \times \Delta E \geq \hbar/2$. However, if wave function overlap is small the wave functions more resemble molecular orbits with well defined, sharp energies. At the same time, the lack of overlap causes low conductivity and the charges spend a long time on the molecules between hops.

The question is if it is really necessary to make them so pure. Again, organic materials are not planned to compete with silicon in performance, but mostly in price. The enhanced performance of the purity will not balance against the extra cost associated with the purification.

Finally, there is a fundamental difference between organic and classical materials in that the latter are more mechanically and chemically stable. In this sense, stability means that the materials do not show phase transitions and that the conduction is by electrons and holes only. In some organic materials, the conduction is by ionic transport, this being a much slower and less controlled process. Phase transitions can also play an important role. Recently it has been pointed out that the omnipresent phase transition in organic materials (see for example the work on sexithiophene [47]) at around 200 K is due to water [48], an impurity very difficult to avoid in the low grade fabrication techniques such as spin coating.

1.2 CONDUCTION MECHANISM

As to the basic conduction mechanism, there is a debate between 'free' carriers (electrons in the conduction band and holes in the valence band) on one side and polarons [49] (or bipolarons [50]) on the other side. A polaron is a charge together with its local lattice deformation and polarization, as shown in Figure 1.1.

It seems most obvious, once the theory from semiconductors has been borrowed, to start assuming free carriers and only introduce polarons when it is not possible to explain the data otherwise. In this work the entities responsible for charge transport are considered to be free carriers, for the sake of simplicity, rather than to make a bold statement about the validity of this assumption. The conduction band, as used in this work might, in fact, be a polaronic band.

Another on-going debate is the distinction between band conduction and hopping conduction (Figure 1.2). In band conduction, the charge is highly delocalized and can travel freely. Charges, however, spend most of their time on localized deep states from where they cannot contribute to current, thus reducing the average mobility. One example of this is Poole–Frenkel conduction, which also includes a field-dependence of mobility, or multi-trap-and-release (MTR), which is equal to Poole–Frenkel with the field dependence removed.

In contrast, in hopping conduction models only localized states exist or play a role, for instance because the delocalized bands are too far

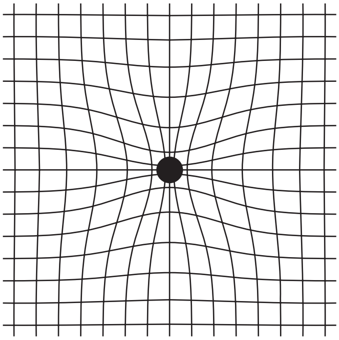

Figure 1.1 A polaron: a charge with its associated lattice distortion

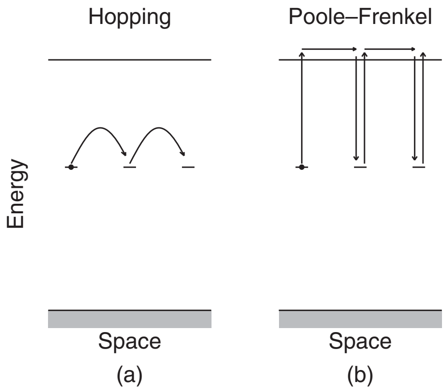

Figure 1.2 Distinction between hopping conduction (a) and Poole–Frenkel conduction (b). In the former charges occasionally jump ('hop') from trap to trap. In the latter carriers spend most of their time trapped but occasionally are excited to the delocalized (conduction or valence) band from where they can contribute to current

away or the temperature too low to allow for thermal excitation of trapped carriers [51]. The charges spend all of their time on these states. Transport of charge occurs by instantaneous hops between these states. This can also cause a field and temperature dependence of the effective mobility, as shown by the simulations of Bässler [45]. Ambegaokar *et al.* [52] extended the work of Mott on hopping/percolation theory that predicts a dependence of conductivity on temperature of the form $\sigma \propto \exp[-(T_0/T)^{1/4}]$. Often, the percolation theory of Shklovskii and Efros is applied to organic materials [53].

Comments by Rakhmanova and Conwell, however, state that Poole–Frenkel conduction seems more likely for organic materials [54]. Also, Waragai *et al.* reject hopping conduction for their transistors because of the unrealistic values found for the parameters [55]. Similarly, Nelson *et al.* reject the idea of hopping conduction for their pentacene transistors [56]. Poole–Frenkel conduction is more adequate for when the devices start having substantial currents and conduction is no longer a perturbation.

Other conduction mechanisms contain a two-band formalism; one conduction band and one defect band [57] (where the designation 'band' for the defect states is somewhat misplaced; they are comparable with the hopping states described above). When the defect band is dense enough, hopping can occur from defect to defect and the associated current can be substantial [58]. This can be nearest-neighbor hopping, or variable-range hopping (VRH) [59, 60].

In this work, a Poole–Frenkel formalism is used. It is assumed that all conduction is through the conduction (and valence) bands with additional efficient traps, deep localized states; to contribute to current, a charge trapped on a deep level has first to be promoted to a conductive band to contribute to current, i.e., no direct hopping from trap to trap is possible. The interesting thing is that the defect band can, in principle, also originate from the polarons. In other words, the traps can be self-traps. A charge can create a lattice distortion that makes it so immobile as to effectively be locked in place, thus behaving like a trap. It would be difficult to explain, though, how it can be that with advances in production techniques, the devices seem to conduct better. After all, a polaron is an intrinsic particle and should not depend much on the quality of the material. However, traps related to impurities such as lattice defects will disappear when going from amorphous to crystalline materials. This difficult discussion is not addressed in this book; no bold statements are made about the exact conduction mechanism. As will be shown, maintaining a two-band formalism with only one band contributing to current, and without stating what the bands represent exactly, will not take anything away from the descriptive power. The discussion about the conduction mechanism is deferred. Many theories exist that are consistent with measured data, yet, the reverse logic cannot be applied, namely that the data are proof of the theory.

As an example of the difficulty of describing amorphous materials consider the analysis of the parameter ‘mobility’, μ. Mobility is probably the most important parameter in electronic materials, as it is directly linked to the switching speed of the devices, because charges either have to drift or diffuse in and out of the active zone of the device and these are both governed by mobility (diffusion via Einstein’s Relation). Switching times are proportional to $L^2/\mu V$, where V is the relevant voltage and L is the relevant device dimension, for instance the channel length in transistors [61, 62]. Therefore, most research is aimed solely at increasing the mobility. Organic materials are often labeled as low-mobility materials. However, we have to be very careful when making such statements. Mostly, the definition of mobility is the basis for the measured low mobility. When we define the mobility as the factor that links current to the product of density of charge (qp, where p is the hole density) and the electric field (E),

$$J = \mu_p q p E \tag{1.1}$$

where J is the current density, it is assumed that we know the density p very well. This assumption is not always true. It is, for instance, often assumed that p is constant, and that all dependencies of the current on temperature are described by a temperature dependent mobility, $\mu(T)$. A more correct picture is one in which the mobility is constant and the charge density is temperature dependent,

$$J(T) = q\mu_{\mathrm{p}}p(T)E. \tag{1.2}$$

Moreover, in the same way, if a material has remarkably low conductivity, this is often not because of low intrinsic mobility, but rather because of unexpected low density of free carriers, for instance because most charge is located on traps and cannot contribute to current. This can be modeled by an effective mobility in which the contributions to current of free and trapped charge are distinguished. The mobility is defined as the proportionality between current and the product of field and *total* charge, $J = \mu_{\mathrm{eff}}\rho E$. This can be written as

$$\mu_{\mathrm{eff}} = \frac{p\mu_{\mathrm{p}} + p_{\mathrm{T}}\mu_{\mathrm{T}}}{p + p_{\mathrm{T}}} \tag{1.3}$$

where p is the density of free charges (holes) in the valence band and p_{T} is the density of trapped charges, μ_{p} is the intrinsic mobility of free holes in the valence band and μ_{T} is the mobility of trapped charges. The designation 'trapped' immediately tells us that $\mu_{\mathrm{T}} = 0$. In this way,

$$\mu_{\mathrm{eff}} = \frac{p}{p + p_{\mathrm{T}}}\mu_{\mathrm{p}} \tag{1.4}$$

or, in other words, the intrinsic mobility μ_{p} is multiplied by the fraction of total charge that is in mobile states. Moreover, since this fraction can be strongly dependent on factors such as temperature or bias, as will be shown in this book, so will be the effective mobility. In conclusion, saying that organic materials have low mobility is inaccurate. One should rather say 'organic materials are trap-ridden'. Moreover, the unfounded assumption of knowledge of the density of charge is often the reason why different measurement methods result in different values for mobility. As examples are the time-of-flight (ToF) and field-effect transistor (FET) mobilities. These two types of measurement normally give widely different results. These measurements will be discussed in this book. As known from elementary physics, not all current is caused by drift. In cases where a gradient of density exists of any quantity, diffusion will try to equalize the distribution and remove the gradient. If these diffusing entities are charged, this results in a current. For holes,

$$J_\mathrm{p} = -qD_\mathrm{p}\nabla p \tag{1.5}$$

where D_p is the diffusion coefficient of holes. An important law in physics is Einstein's Relation, that couples the diffusion coefficient to the mobility,

$$D_\mathrm{p} = \frac{kT}{q}\mu_\mathrm{p} \tag{1.6}$$

where the proportionality factor is called the thermal voltage, known from electronics, and is equal to 26 mV at room temperature. The total hole current in the one-dimensional case, with current along the direction x, thus becomes

$$\begin{aligned} J_\mathrm{p} &= -qD_\mathrm{p}\frac{\partial p}{\partial x} + q\mu_\mathrm{p}Ep \\ &= q\mu_\mathrm{p}\left(pE - \frac{kT}{q}\frac{\partial p}{\partial x}\right) \\ &= \mu_\mathrm{p}p\frac{\partial E_\mathrm{F}}{\partial x} \end{aligned} \tag{1.7}$$

where the last step is easily demonstrated if we assume that the carrier concentration depends exponentially on the Fermi level, $p = \exp[(E_\mathrm{V} - E_\mathrm{F})/kT]$ and $\partial E_\mathrm{V}/\partial x = q\partial V/\partial x = -qE$. The interesting fact is that for many disordered materials, the Einstein Relation is violated and the relation between diffusion coefficient and mobility can be much larger than 26 mV, even way beyond the small correction factor of $1 + 0.35p/N_\mathrm{V}$ as given by Sze for classical semiconductors [9]. As will be shown, this can have tremendous impact on the behavior of the devices.

1.3 CHEMISTRY AND THE ENERGY DIAGRAM

Where the basic ingredient of organic materials is the carbon atom, the basic ingredient of organic semiconductors is conjugation. Conjugation is a chain of carbon atoms with alternating single and double bonds, as shown in Figure 1.3. This has two important results, namely the

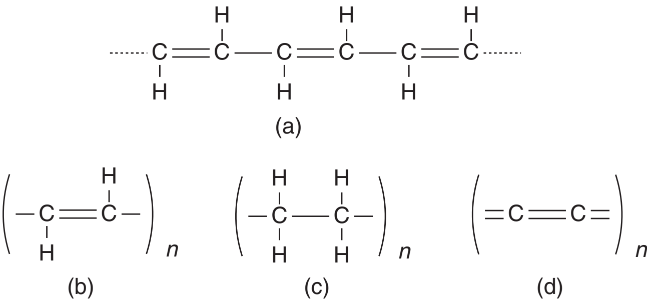

Figure 1.3 (a) The principle of conjugation in organic electronic materials shown in Lewis structures. Conjugation consists of a chain of carbon atoms with alternating single and double bonds. Note that any of the hydrogen atoms can be replaced by a functional side group, for instance to make the compound soluble. (b) The simplest organic polymeric semiconductor, polyacetylene. (c) The nonconjugated equivalent, polyethylene. The difference in room-temperature conductivity between polyethylene and polyacetylene is about seven orders of magnitude. (d) Polyallene with only double bonds also has relatively low conductivity

opening of a band gap, a splitting of the energy levels, in the range of semiconductors, and the delocalization of charge in these levels. Figure 1.4 shows examples of organic semiconductor materials in which the chain can easily be recognized.

The four electrons on each carbon atom in the chain can be considered to reside in sp^2 hybridized orbitals (3) and in a p_z orbital (1). The three sp^2 electrons are used to form covalent bonds via σ molecular orbitals to neighboring carbon atoms in the chain on either side and to the sidegroup (for instance a simple hydrogen atom). The remaining electron in the p_z orbital is then used in a covalent bond via a π molecular orbital with a neighboring carbon atom in the chain on one side only. The result is a chain of alternating single (σ only) and double (σ and π) bonds. Figure 1.5 shows the energy diagram of an interaction between two carbon atoms forming a double bond. After filling the levels from low to high (using Hund's Rules for the spins [63]) it can be recognized that four electrons (two from each carbon atom) are used in bonding, two in σ_- molecular orbitals, and two in π molecular orbitals. The remaining four electrons are in nonbonding (nb) orbitals and are still available for bonding to the rest of the chain and the ligands. The basic feature is the splitting between the π and π^* molecular orbitals caused by the interaction between the p_z atomic orbitals. Interactions between p_z orbitals further away in the chain cause additional, smaller splittings of the levels, as schematically indicated in Figure 1.5(b). A highest occupied

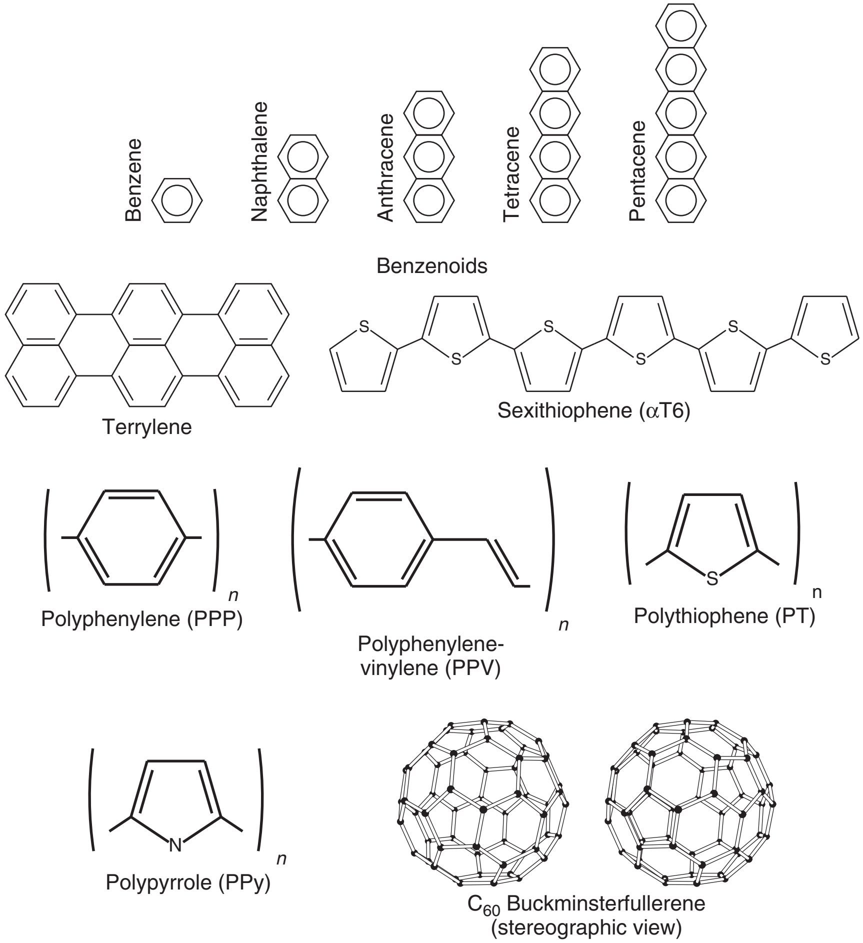

Figure 1.4 Examples of organic semiconducting materials, divided into oligomers and polymers. In each one a chain of alternating single and double bonds can be recognized as in Figure 1.3. The benzenoids (for example, tetracene) are pure carbon-hydrates with fused hexagon structures, such fused rings giving rigidity to the molecules. For phenylenes, the rings are separated, in PPP by a single bond and in PPV by a short conjugated link of two carbon atoms. Both are shown here in the para form (with the links in opposing sites of the benzene ring). The basic structure in thiophenes is a pentagon ring with in each ring one carbon atom replaced by a sulfur atom. Likewise, in pyrroles a carbon atom is replaced by a nitrogen atom. More complex structures include terrylene and buckminsterfullerene (shown in stereographic view), the latter being a purely carbon molecule in which each atom is bound to three neighbors, i.e. has one double bond. For all but buckminsterfullerene, the convention of organic chemistry is used whereby carbon atoms are not shown and neither are hydrogen atoms nor bonds with hydrogen atoms

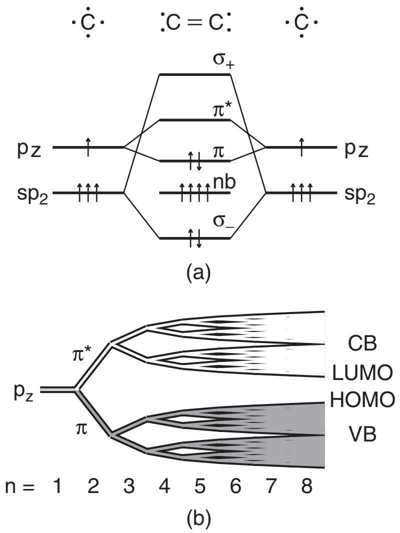

Figure 1.5 (a) Energy diagram of two interacting carbon atoms. sp_2 and p_z atomic orbitals of the two individual carbon atoms combine to form π, σ and nonbonding molecular orbitals. (b) A band structure starts emerging with a narrowing band gap when the conjugation length of alternating single and double bonds is increased. A HOMO and LUMO can be recognized that is part of the valence band (VB) and conduction band (CB), respectively

molecular orbit (HOMO, π) and lowest unoccupied molecular orbital (LUMO, π*) can be recognized.

The formation of a chain of single and double bonds thus causes an energy structure with a HOMO and a LUMO level, with a splitting ('band gap') in the range of semiconductors. From Figure 1.5 it is also clear that a material with only single σ bonds, like polyethylene, will have a much wider band gap and will not easily fall in to the category of semiconductors. The same goes for polyallenes with only double bonds (Figure 1.3d). To result in a semiconductor material, conjugation is essential.

For polymeric organic electronic materials, the size of the chain of alternating single and double bonds is, in principle, infinite. For oligomeric organic materials, the chain is limited to the molecule. Figure 1.6 shows for the specific case of benzenoids how the increasing chain length causes a narrowing of the band gap E_g [64]. For polymer chains, a similar effect of the HOMO–LUMO splitting as a function of chain length has been calculated [65]. In any case, often the term 'conjugation length' is used to designate the length, or average length,

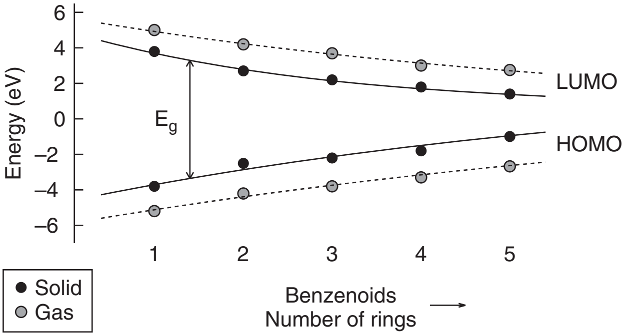

Figure 1.6 Band gap E_g as a function of molecular size in benzenoids. For increasing conjugation length, from benzene to pentacene, the gap narrows. This effect is caused by increased dislocation of the charges and is further amplified when the molecules are close to each other in solids. After Karl [64]

of uninterrupted chain. Figure 1.6 also shows how the band gap is further narrowed when the molecules are placed in the solid state form caused by van der Waals interactions between molecular orbitals on near molecules.

For many molecules, the place of the double and single bonds is not uniquely determined, but has two distinct configurations with exactly the same energy. In these cases, resonance of the two forms causes a dislocation of the electrons; it is no longer possible to identify the place of the single and double bonds, see Figure 1.7; the electron wavefunction becomes one continuous cloud. For other materials, for instance the linear chains with an odd number of atoms, the different forms have slightly different energies, but the difference is small enough to allow for this dislocation effect. In any case, this dislocation effect is essential for conduction. A charge injected into a π molecular orbit can relatively easily migrate along the chain, as demonstrated by Figure 1.8. Often the description 'electron-relay' is used to visualize the current. This seems quite adequate as the passing of charge is similar to a long line of people passing each other buckets of water in order to put out a fire.

Figure 1.7 Resonance between the two equal-energy configurations of single and double bonds causes dislocation of the charges. In aromatic compounds this is shown by a ring in place of indicating the location of the double bonds

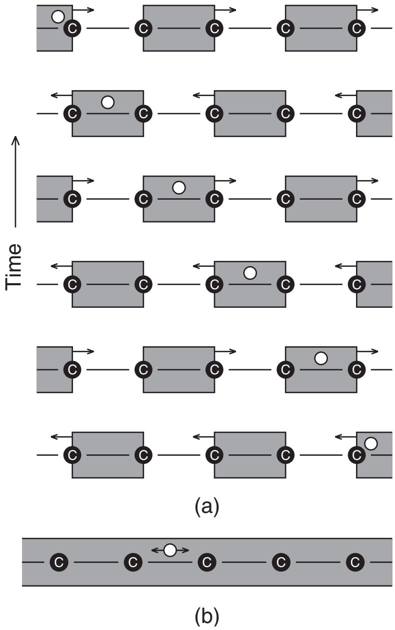

Figure 1.8 (a) Schematic time sequence showing how resonance between two configurations of alternating single (indicated by lines) and double bonds (gray rectangles) gives a way for a charge (indicated by a white circle) injected into a π molecular orbit to travel along the chain. The π molecular orbits are represented by gray planes. The arrows indicate how the positions of double bonds change in a transition from one state to the other. On account of the high rate of transitions between the two resonant states, it is better to think of the system as a single, continuous, highly delocalized wavefunction as in (b)

For limited conjugation lengths, macroscopic conduction is then made possible by further overlap of molecular orbits with neighboring molecules, causing so-called Davydov splitting of the molecular levels. Figure 1.9 summarizes the intramolecular interactions causing molecular orbits and inter-molecular interactions further dispersing the energy levels, and delocalizing the electrons. The interactions cause the wavefunctions with maximum same-sign overlap to have lowest energy and those with proximity of opposite-sign parts to have highest energy. Half of the electronic states are occupied (each p_z orbital contributes one electron and in each electron wavefunction fit two electrons, with opposing spin directions) and in this way a HOMO and LUMO can be identified. When the splitting between these two levels is relatively small, *and* a large delocalization of the electrons occurs, a semiconductor results. In this case it is better to use the jargon of semiconductor physics

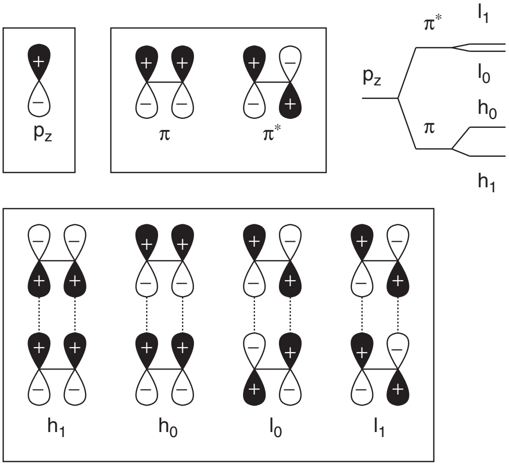

Figure 1.9 Intramolecular interactions between p_z electrons causing molecular orbits π and π^*. Additional (intermolecular) interactions cause a further spreading of the electronic levels. The interactions make the wavefunctions with maximum same-sign overlap to have the lowest energy, in this case h_1 and the wavefunction with maximum opposite-sign overlap to have the highest energy, in this case l_1. Half of the levels are occupied and this causes the distinction between HOMO and LUMO (in this case h_0 and l_0, respectively)

and replace the chemistry words ‘HOMO’ and ‘LUMO’ by ‘valence band’ and ‘conduction band’, respectively. In this language, we can say that an electron is promoted from the top of the valence band (VB) to the bottom of the conduction band (CB). Both the electron in the CB (LUMO) and the missing electron, or ‘hole’, in the VB (HOMO) can nearly equally well contribute to current. In practice, most organic semiconductors conduct better via holes because of a higher efficiency of trapping (immobilizing) electrons.

To summarize, the overlap of atomic and molecular wave functions causes a dislocation of electrons and the formation of valence and conduction bands. For materials on the insulating side of the spectrum, the overlap is minimal and the molecular orbitals (LUMO/HOMO) are good designations, whereas for the semiconducting materials, the overlap is strong and it is better to talk about ‘conduction band’ and ‘valence band’. The time a charge spent on an individual molecule is minimal and the accompanying level broadening ΔE is large, further blurring the molecular levels. In these cases, electronic band structures can be calculated, see for instance the calculations on crystalline pentacene [66]. (Note that materials do not have to be crystalline to have semiconductor