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The Electronic Structure of Organic Semiconductors

1.1 Introduction

Organic semiconductors are a class of materials that combine the electronic advantages of semiconducting materials with the chemical and mechanical benefits of organic compounds such as plastics. Thus, the ability to absorb light, conduct electricity, and emit light is united with a material structure that can easily be modified by chemical synthesis, for example, to tailor electronic properties such as the desired emission wavelength, to render it soluble, or to allow for mechanically robust, lightweight, and flexible thin films. These properties imply that semiconductor applications such as displays, lighting panels, or solar cells may be produced with a variety of solution-processing techniques or vacuum deposition methods (Figure 1.1).

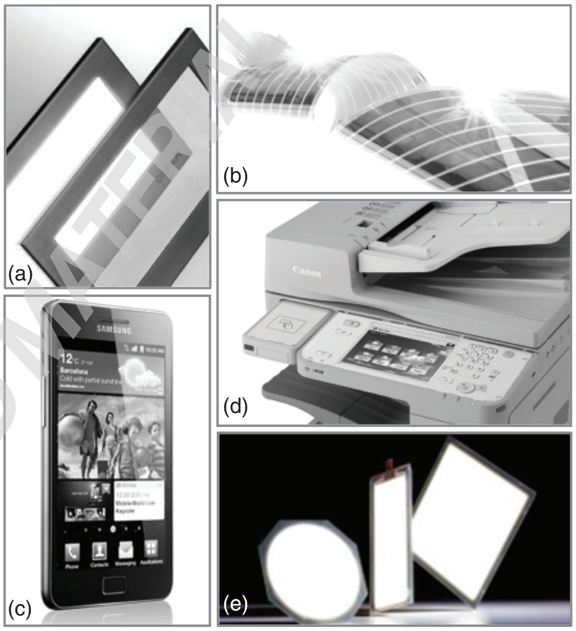

Figure 1.1 Examples of future and present organic semiconductor applications. (a) Prototype for a luminescent window made with an organic electroluminescent semiconductor. When switched off, the window provides a view to the outside, yet when switched on, it emits light, thus functioning as panel lighting. (From OSRAM with permission.) (b) Prototype for a continuous, flexible solar cell foil employing an organic semiconductor (Konarka Power Plastic® by George Disario). (c) Commercially available Samsung Galaxy smartphone featuring an OLED display. (d) A photocopier using organic semiconductors for the xerographic process by Canon. (e) Commercially available lighting tiles by OSRAM.

The technological exploitation is, naturally, in a constant flow of development. The large-scale exploitation of organic semiconductor materials in the xerographic process of photocopier machines in the late 1970s, and later on in laser printers, brought organic semiconductors into any typical office. Today, displays based on organic light-emitting diodes (OLEDs) are omnipresent. Companies such as LG, Samsung, and Xiaomi use OLEDs for their TV and smartphone products. Developments such as TVs that are rollable employ the soft nature of organic semiconductors to their advantage, and transparent TVs have been demonstrated. Smartphone displays are meanwhile routinely fabricated with OLED displays, with foldable displays representing more recent developments. Organic solar cells (OSCs) are entering niche markets such as building-integrated photovoltaics where OSC foils bring the advantage of being lightweight [1]. Thus, in addition to established products, there is a constant flow of ideas for novel, innovative products that needs to be evaluated.

Over the last decade, the field has seen a keen interest in applications at the interface to biological systems. This includes bioelectronic devices and biosensors [2]. For example, organic field-effect transistors (OFETs) can be printed at small sizes on stretchable, thin foils that render organic electronics compatible with biological interfaces [3]. This allows for applications in the area of on-skin wearable electronics, typically used for sensing physiological signals with relevance to human healthcare such as temperature, electrolytes, metabolites, and pH value [4, 5]. Implantable electronics and electronic interfaces to neurons are also envisaged [2]. An already well-advanced example of implantable electronics is retina prosthetics. Retinal dystrophy is a disease that causes loss

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of vision because the photoreceptors in the human eye, i.e. cones or rods, lose their function. As a follow-on from research into OSCs, researchers demonstrated that the organic semiconductor poly(3-hexylthiophene) (P3HT) can be used as a replacement that works successfully in trials with rats. In several stages, the work evolved from OSC-like structures to subretinal implants made of soft silk and then to simply injecting P3HT nanoparticles into the retina, thus even eliminating the use of surgery [6–10].

Many of the bioapplications exploit not only the soft nature of organic semiconductors but also the fact they can be made to exhibit mixed (both ionic and electronic) conductivity if required. This makes them an ideal interface between ionic-mediated biological systems and electronic-mediated device circuits. Overall, it is evident that there is a large industry involved in the present day and in the future exploitation of organic semiconductors. Consequently, there is also a need for highly qualified personnel familiar with the conceptual premises that govern electronic processes in organic semiconductors.

Over the last decade, the number of research groups that are active in the field of organic semiconductors has increased strongly. Summer schools, graduate training programs, and advanced lecture courses, typically in the context of an MSc degree or PhD, aim to educate students in many aspects of this field. With this book, we wish to contribute to this process by providing a basic and broad introduction to organic semiconductors that should enable the reader to explore different aspects of this fascinating field later on independently in more depth.

1.1.1 What Are "Organic Semiconductors"?

The term "organic semiconductors" implies (i) that the materials are mostly made up of carbon and hydrogen atoms, with a few heteroatoms such as sulfur, oxygen, and nitrogen included, and (ii) they show properties typically associated with a semiconductor material. The latter means absorption and emission of light in the visible spectral range and a degree of conductivity that is sufficient for the operation of classical semiconductor devices such as light-emitting diodes (LEDs), solar cells, and field-effect transistors (FETs). While they show semiconducting properties, one needs to understand that the semiconducting nature differs between inorganic and organic materials.

The atoms that make up inorganic semiconductors such as silicon (Si), germanium (Ge), or gallium arsenide (GaAs) are joined by strong covalent bonds. These bonds may also carry some ionic character, as in GaAs, yet in any case, they allow for a delocalization of the involved electrons over many atoms, resulting in the formation of wide electronic bands (with bandwidths exceeding 1 eV). This electron delocalization implies that charges are highly mobile, with electron mobilities above 1000 cm^2/Vs resulting from coherent charge transport. Charges readily move when an electric field is applied, which finds its expression in a high value of the dielectric constant of around $\varepsilon_r = 11-12$. Interactions between charges such as Coulomb or exchange interactions are therefore well shielded. As a result, light absorption in an inorganic semiconductor creates an electron in a conduction band and a hole in a valence band that are not bound by Coulomb interactions and that are both well delocalized over many atoms.

In contrast, the molecules that constitute an organic semiconductor material are kept together by weak bonds of a van der Waals type. The bonds can have further contributions by hydrogen-bonding interactions or ionic interactions. The weak interaction between adjacent molecules implies that the delocalization of electrons across several molecules is poor. Bands may form in crystalline structures at low temperatures, yet they are only a few 100 meV wide and are reduced or even destroyed by lattice vibrations upon heating to room temperature. In amorphous structures, electrons are localized onto the molecular constituents. This implies that charges move between molecular sites by incoherent, thermally or field-assisted tunneling (*hopping*). This is a slow process, resulting in mobilities well below 1 cm^2/Vs, with values often around 10^{-4} cm^2/Vs. This also prevents a significant electron redistribution in response to an electric field, i.e. electric screening is poor as expressed by a low dielectric constant of $\varepsilon_r = 3-4$. As a consequence, electron–electron interactions of a Coulomb or exchange type are not negligible but rather dominate much of the photophysics in organic semiconductors. Light absorption creates an excitation that is localized to the molecular site and that may be described as a strongly coulomb-bound electron–hole pair (*exciton*). A Coulomb binding energy of about 0.4–1.0 eV separates it from the energy of a free electron and hole, i.e. an excess electron on one molecule and a missing electron on another molecule far away. The differences between organic and inorganic semiconductors are expounded in more detail in Section 2.5.

The brief exposition given here may be sufficient to illustrate that equations, commonly, found in textbooks on inorganic semiconductors, may not always apply to organic semiconductors. Such equations are often based on assumptions related to the high charge mobility and dielectric screening that prevail in inorganic semiconductors, yet break down in organic semiconductors. Hence, in order to understand and quantitatively describe the photophysics of organic semiconductors, knowledge of their electronic structure is required. This is even more the case if one wishes to design and improve organic semiconductor devices.

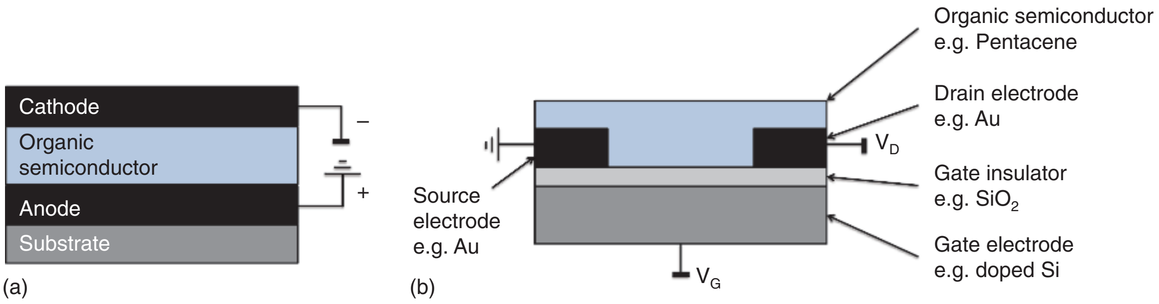

Figure 1.2 Cross-section of basic typical organic semiconductor devices. (a) Diode (OLED or OSC), (b) field-effect transistor (OFET). Basic structure of an organic field-effect transistor (OFET).

Optoelectronic devices made from organic semiconductors are used in a wide range of electronics applications, from photocopiers, laser printers, mobile phones, and TV displays to building-integrated photovoltaics, biomedical sensing, and healthcare electronics. The most common device architectures are the diode and the transistor (Figure 1.2). In the most simple diode structure, a 100-nm film of organic semiconductor is sandwiched between two electrodes, with the bottom electrode being transparent and on a substrate. This makes it a two-terminal device. A typical substrate is a glass, covered with indium tin oxide as an electrode. The organic semiconductor is deposited onto it from a solution or thermally evaporated, and a top electrode such as aluminum can be thermally evaporated to complete the device. Applying a voltage injects positive and negative charges that move through the semiconductor film. Although some charges might exit the organic film at the counter electrode, only generating dissipated heat, part of the electrons and holes will meet, thus creating an excited state that can recombine to the ground state with or without light emission. If the light emission is strong, the diode can be used as OLEDs, e.g. for mobile phones or TV displays. The same diode structure, yet with the inverse process, can be employed to make OSCs. The organic semiconductor film absorbs incident light to generate excited states, of which some may split into free, mobile positive and negative charges. These charges then move to opposite electrodes, where they are gathered to produce a current. The second fundamental device structure is the transistor, most commonly as an FET. It is a three-terminal device with a source and drain electrode on either side of the organic semiconductor film. This is placed on top of an insulating layer that separates the semiconductor from a gate electrode. When a potential is applied to the gate electrode, a current can flow between the suitably biased source and drain electrodes. This current moves in a very thin layer of the semiconductor, adjacent to the insulator layer.

The operation of these devices requires the injection, transport, and extraction of charges. Light absorption or emission can be important, as well as recombination or dissociation of charges. This brief exposition on the operation of OLEDs, OSCs, and OFETs may suffice to illustrate the need for a detailed and more profound understanding of the underlying photophysical processes.

It is useful to distinguish between three varieties of organic semiconductors, which are

(I) *Amorphous molecular films*: By this term, we mean organic low-molecular-weight molecules deposited as an amorphous film through evaporation or spin-coating. Thin (100 nm) amorphous films of molecules are employed for device applications such as LEDs, and molecularly doped polymer films are used on a large technological scale in xerography.

(II) *Molecular crystals*: A crystal consists of a lattice and a basis. In the same way how atoms like silicon can form a crystal by covalent bonding, or sodium and chloride atoms by ionic bonding, molecules such as naphthalene or anthracene can form the basis of a crystal that is held together by van der Waals interactions. The charge mobilities that can be obtained in molecular crystals are high (up to a few cm^2/Vs) compared to those in noncrystalline organic materials (on the order of 10^{-4} cm^2/Vs). This renders crystalline molecular structures relevant for transistor applications.

(III) *Polymer films:* Polymers consist of covalently coupled molecular repeat units. Their high molecular weight precludes deposition by evaporation. Rather, they are processed from solution, which allows for a range of deposition techniques including simple spin-coating, ink-jet deposition, or industrial reel-to-reel coating. They are more suitable for blending than molecules since polymer blends are thermodynamically more stable and less susceptible to crystallization.

The semiconducting properties of these types of organic semiconductors have a similar origin, though their excited states and associated photophysical properties vary slightly depending on the order and coupling in the solid. As shall be detailed further below, the semiconducting nature is associated with the energy levels of the prevailing π-electrons. In this book, it is understood that we refer to molecules and polymers with extended π-orbitals unless stated otherwise.

1.1.2 Historical Context

It is useful to have a little background on the origins of this research field to place the available literature, be it books or journal articles, into context. This field comprises researchers who come from different disciplines, schools of thought, and traditions, and the interpretation of experimental results is usually based on the background a researcher has.

One of the roots goes back to the field of **molecular crystals**. The first studies on conductivity, photoconductivity, the photoelectric effect, and the fluorescence of organic solids have already been reported at the beginning of the twentieth century [11–14]. Even electroluminescence had already been reported as early as 1953 by Bernanose on a cellulose film doped with acridine orange [15]. The main period of research on molecular crystals such as naphthalene and anthracene, however, took place in the years from 1950 to 1980. This field gained momentum from the report of electroluminescence in an anthracene crystal by Pope in 1963, and Helfrich and Schneider in 1965 [16–18]. Unfortunately, molecular crystals, held together by van der Waals forces, are brittle and thus require a certain minimum thickness in the range of a few μm. This implies that the electric field needed for charge injection and conduction can only be obtained by applying a few 100 V across the crystal slice. Clearly, this is not suitable for any consumer application. Lower operating voltages were made possible with the adventure of 100 nm thin films made from amorphous vacuum-deposited molecules and from spin-coated polymers [19, 20]. As a consequence, research interest moved on to amorphous organic materials and the concepts developed originally for molecular crystals were transferred to amorphous films. Central ideas that have their origin in the field of molecular crystals are the notion that charge carriers can move in a narrow band at low temperatures in a defect-free crystal, yet that coherence is destroyed at higher temperatures so that charges move by hopping between molecules at room temperature. A further key concept is that optical excitation in a molecular crystal creates a Coulomb-bound electron–hole pair, termed a *Frenkel exciton*, that may move through the crystal. These ideas are well explained in the book by Pope and Swenberg [21] and in the book by Schwoerer and Wolf [22].

Another source of concepts underpinning organic semiconductors lies in the field of **molecularly doped polymers (MDPs)**. When companies such as Xerox and Kodak investigated materials that are suitable as photoreceptors for electrophotography in the mid-1970s, it was noted that the until-then used inorganic chalcogenides such as As_2Se_3 could be replaced profitably with a few μm-thin film of MDPs. The application of xerography requires a material that has a very low dark conductivity yet a reasonable photoconductivity. This is well fulfilled by MDPs, which consist of an inert polymeric binder material, e.g. polycarbonate, that is doped with about 30% by weight of an optically active molecule such as triphenylamines. MDPs have the advantage of being nontoxic and easy to process, and for this reason, they are still used in every common photocopying machine today. For this application, it was essential to understand how charge is transported between different molecules. Key concepts for *charge transport by hopping* evolved in this context [23]. A good introduction to this field can be found in the book by Borsenberger and Weiss [24].

The field of organic semiconductors was also influenced significantly by the discovery in the late 1970s that high conductivities could be obtained in π-conjugated polymers, i.e. hydrocarbon chains with alternating single and double bonds, when they are doped. Oxidative or reductive doping by halogens or alkali metals, respectively, raised the conductivity by 10^9 orders of magnitude to values even exceeding 10^5 S cm^{-1}. The discovery and development of these **conductive polymers** were rewarded in 2000 with the Nobel Prize in Chemistry to Heeger, MacDiarmid, and Shirakawa [25, 26]. Early interpretations of the electronic structure of the *doped polymers* were giving strong weight to polaronic effects, i.e. the fact that the bond lengths in a polymer chain change when a charge is placed on the polymer while neglecting electron–electron interactions [27, 28]. In the course of time, however, it became clear that Coulomb and exchange interactions between charges are so significant in π-conjugated polymers that they cannot be disregarded, while polaronic effects are modest. In fact, *Coulomb and exchange interactions* were found to be central for a suitable and correct description of the electronic structure. The lively scientific debate that eventually led to this insight is portrayed, for example, in the book edited by Sariciftci [29]. The early atomic dopants tended to diffuse out of the sample in the course of time. Today, a wide range of molecular dopants are in use that provide long-term stability [30].

The technological development of organic semiconductors took off with the discovery of electroluminescence in about 100 nm thin **amorphous organic films**. In 1987, Tang and Van Slyke reported an amorphous thin-film LED made with the molecule Alq_3 with an external quantum efficiency of 1% (emitted photons to injected electrons), a high value at the time [19]. The low film thickness implied that the necessary electrical field was already obtained for voltages below 10 V, significantly lower than in the case of molecular crystals. The abstract of their paper declares "High external quantum efficiencies (1% photon/electron), luminous efficiency (1.5 lm/W), and brightness (>1000 cd/m^2) are achievable at a driving voltage below 10 V." This was followed in 1990 with the report of electroluminescence below 14 V in a 100-nm-thick film of the nondoped π-conjugated polymer PPV by Friend and coworkers [20]. The report of *low-voltage electroluminescence* was a breakthrough that caused a paradigm shift. The operation at low voltage implied a wide technological potential for organic semiconductors, starting from the display sector. Thus, the focus in the scientific community shifted from fundamental studies to application-oriented studies, and the entire field gained an enormous drive. From a technological perspective, the two types of materials, amorphous molecules and polymers, differ in the way how they are processed into films. While the light-emitting molecules are mostly deposited by vacuum evaporation, the polymer films are fabricated by spin-coating from solution.

The observed electroluminescence, and later on any related optoelectronic properties such as field-effect mobility in transistors or photoconductivity in solar cell structures, was interpreted using elements from the three established fields described above. For example, it became soon evident that charge transport is best described by the concept of hopping established for MDPs. Further, for amorphous molecular films, the excited state was, and still is, frequently referred to an exciton as in the case of a molecular crystal. Strictly taken, this is not correct, and the term exciton should only be used in the context of a highly ordered system, though an unfortunate tradition has evolved of using "excitation" and "exciton" as synonyms. Finally, the importance of electron–electron interactions in the description of organic semiconductor physics is meanwhile well established [31]. The technological exploitation of this semiconductor class is also well underway and evident in any large electronics shop selling OLED TVs. For an overview of the history of OLEDs, we refer to Hong *et al.* [32].

This context warrants a mention of the publications by Jan Hendrik Schön in the early 2000s from AT&T Bell Laboratories. In a series of papers published by high-impact journals such as *Nature* and *Science*, he claimed major discoveries at an unprecedented rate of about one article per week. The fact that other labs could not reproduce his results was initially attributed to difficulties in sample preparation such as issues with sample purity. With increasing time, however, it raised suspicions, until eventually it became evident that some of the reported data was made up. (The fraud became transparent when scientists noticed that some figures that were supposed to report very different quantities were actually showing identical data, even down to having the same background noise. When confronted, Schön claimed data confusion yet could not show the original raw data.) This prompted major discussion in the scientific community on the responsibilities of authors, referees, and supervisors, as well as on the duty to keep documentation of experiments and resulting raw data. Part of today's obligation to scientific data storage results from this experience.

1.2 Different Organic Semiconductor Materials

For a first orientation, we list here some examples of the three different classes of organic semiconductor materials. Note that chemical structures are also listed in the appendix.

1.2.1 Molecular Crystals

A straightforward place to start are molecular crystals. Like any crystal, they are characterized by a perfectly ordered point lattice and a basis, i.e. the structural unit that is placed at the lattice point. In an inorganic crystal like silicon or germanium, the basis is formed by atoms, while molecular crystals have a basis formed by molecules. Typical crystal-forming molecules are flat, large, aromatic molecules such as polyacenes, in particular naphthalene, anthracene, tetracene, and pentacene, as well as pyrene, perylene, and similar compounds (see Figure 1.3). These molecules have filled valence orbitals, and they are electrically neutral. Whereas a silicon crystal is kept together by covalent bonds formed between only partially filled orbitals of the atoms, and a sodium chloride crystal takes its cohesion from ionic bonding between the charged Na^+ and Cl^- ions, these forms of strong bonding are not available to a molecular crystal. Instead, the attractive force between the neutral and nonpolar molecules is provided by comparatively weak van der Waals interactions.

The concept of the van der Waals interaction between two molecules is based on the fact that molecules that have no static dipole moment still have a charge distribution that is not entirely rigid. A temporal fluctuation in the charge distribution in a molecule implies an associated temporary fluctuating dipole moment. This will induce a corresponding fluctuating dipole in the second molecule.

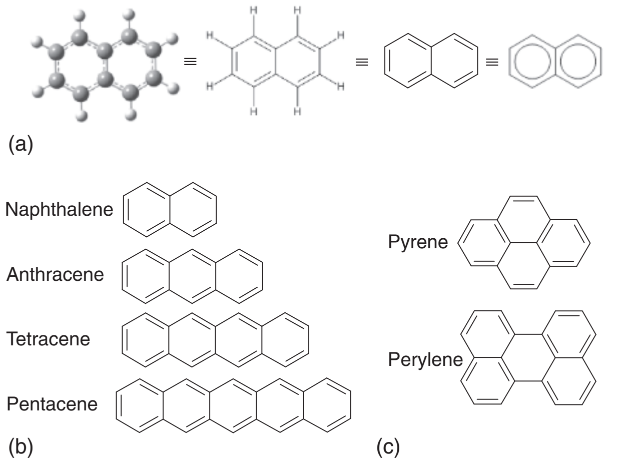

Figure 1.3 Chemical structures of π-conjugated molecules that tend to form molecular crystals. (a) The structure of naphthalene, explicitly including the H-atoms. In any subsequent figure, the H-atoms shall be omitted as is custom in the field. (b) The structure of the acenes from naphthalene to pentacene. (c) The structures of the molecules pyrene and perylene.

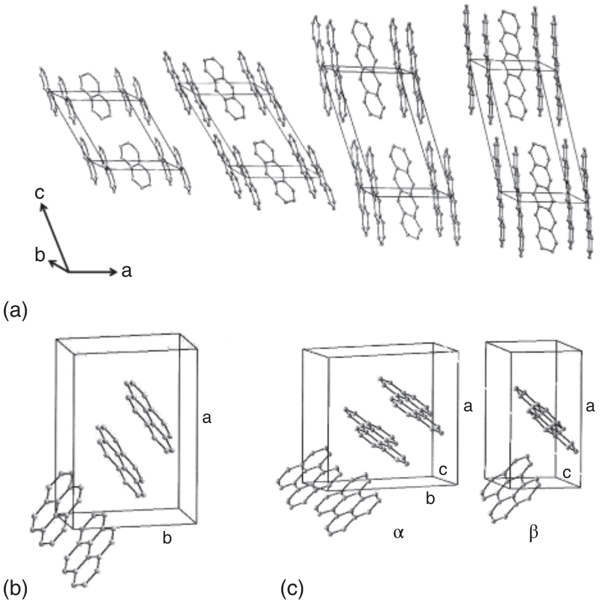

Figure 1.4 Typical crystal structures of organic molecular crystals [22]. (a) The unit cell for the naphthalene, anthracene, tetracene. and pentacene. The crystal has a simple cubic lattice with a basis consisting of two molecules that are arranged in a herringbone stacking, i.e. the H-atoms of the second molecule point toward the π system of the first molecule. (b) The unit cell for pyrene. Only the simple cubic lattice and the basis is shown. The basis consists of four molecules, i.e. two sandwich-type pairs arranged in a herringbone manner. (c) The unit cell for perylene in two different phases: the α phase and the β phase. Only the simple cubic lattice and the basis is shown. In the α phase, the basis comprises four molecules analogous to pyrene, while in the β phase, the basis is made up of two molecules in herringbone stacking.

The electrostatic interaction between the correlated fluctuating dipoles in the two molecules results in an attractive force, the van der Waals attraction. This force depends strongly on the distance r between the molecules, and on the ability to induce dipole moments in a charge distribution, i.e. the polarizability α of a molecule. Quantitatively, the potential energy associated with a van der Waals interaction is given by $V_{\mathrm{VdW}} \propto \alpha^2/r^6$, i.e. the force is proportional to r^{-7}, as elaborated in Chapter 2, Section 2.1 [22].

This has two consequences. First, the dependence on polarizability implies that molecular crystals are preferentially formed by molecules that possess a filled valence orbital that is large and delocalized so that many electrons can easily be moved over some distance on the molecule. As we shall detail further below, this is the case for flat molecules with π-orbitals, like the polyacenes. In fact, the increase in polarizability explains why the melting points of the polyacene molecular crystals rise with their size (benzene 5.5 °C, naphthalene 80 °C, anthracene 216 °C, and tetracene 357 °C) [22]. Second, the strong distance dependence of the comparatively weak van der Waals forces leads to tightly packed structures (Figure 1.4). A particularly frequent structure is the herringbone arrangement (see Figure 1.4). This structure is further assisted by electrostatic interactions between the comparatively electron-deficient hydrogen atoms in the polyacene and the electron-rich π-electrons of the aromatic ring system. Other common packing motifs include slipped stack and brick wall packing [33].

Usually, the crystal structure is made up of individual molecules, as is the case for naphthalene or for the β-phase perylene. It can, however, also occur that it is made up of a weakly interacting pair of two identical molecules, as is the case for pyrene and for α-phase perylene (Figure 1.4c). Since the pair is only weakly bound, it absorbs as a monomer, yet it emits as a dimer. This is referred to as excimer emission. There are a number of monographs available on the subject of molecular crystals, to which the interested reader may refer for more detail [22, 34–36].

Today's technological interest in molecular crystals arises mostly from the field of OFETs. For OFETs, the total thickness of the organic semiconductor is not relevant, while the mobility of the charge is important to yield reasonable switching times of the OFET. Thus, the high degree of order that prevails in molecular crystals and that allows for comparatively high charge mobilities render them of interest for OFET applications, even though their preparation can be demanding. OFETs employing crystalline materials were reported reliably with hole mobilities in the range of 1–15 cm^2 V^{-1} s^{-1} [33]. There exist reports of apparently higher mobilities, though these are frequently the result of unsuitable data analysis when the OFET transfer characteristics are nonlinear [37, 38]. For OFETs, the crystals are typically grown directly on the substrate, using sophisticated evaporation or solution deposition techniques. Besides single crystals, polycrystalline films are also used, though their performance is limited by grain boundaries between crystalline domains. A relevant parameter for OFET application is not only the purity and structure of the crystalline material but also the orientation of the molecules relative to the insulator surface (and thus also relative to the source and drain electrode) [39], as charge transport in molecular crystals is highly anisotropic [21, 22].

1.2.2 Amorphous Molecular Films

With this class of materials we associate molecules that form amorphous films, i.e. glasses, that are suitable for organic semiconductor applications. For those new to the field of organic semiconductors, and in particular to those with a background outside chemistry, the wealth and variety of chemical structures they encounter may at first seem overwhelming. After a short inspection, the beginner may notice that most molecules they encounter are made up of similar chemical units, usually phenyl rings, some five- or six-membered rings with heteroatoms like sulfur, nitrogen, or oxygen in it ("heteroaromatic rings"), and occasionally a few carbon atoms, either with alternating single and double bonds when in the center of the molecule, or with a sequence of single bonds when forming a side chain. For the nonchemists, an overview of frequently encountered chemical units and their names is given in the appendix.

Scientists and companies who synthesize molecules for organic semiconductor applications tend to distinguish between the molecules according to their processability or according to their function in the device. This tends to be a useful way to order the large number of compounds that are available, and we shall employ this approach to exemplarily introduce some of the commonly used compounds.

When considering processability, one differentiates between molecules that are deposited by evaporation in a vacuum and those that are deposited on a substrate by spin-coating after dissolving them in a common organic solvent such as toluene, chloroform, or chlorobenzene. For vacuum deposition, the compound needs to sublime upon heating before it decomposes. Good thermal stability can often be obtained by including intrinsically stable aromatic rings in the chemical structure and by avoiding side chains, which are more likely to break up. In contrast, for spin-coating, solubility needs to be high, and this requires the use of solubilizing groups such as side chains. Thus, the same chemical moiety can, in principle, be prepared in a version for either processing method, depending on whether and to which extent solubilizing groups are incorporated in the chemical structure. Examples of such molecules are given in Figure 1.5. The need to keep the

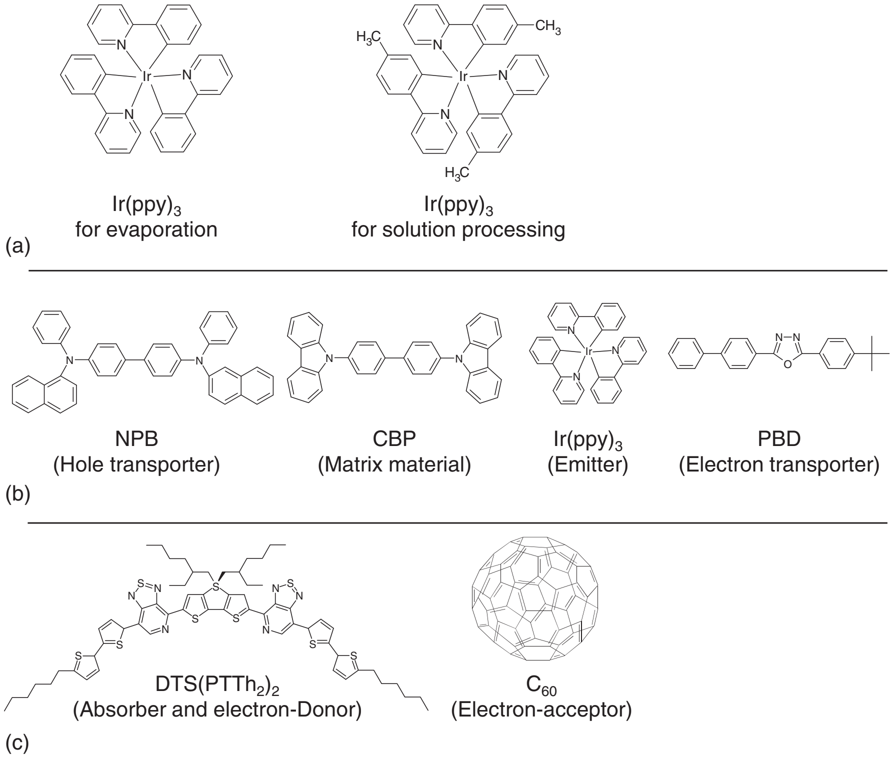

Figure 1.5 Examples and classification of π-conjugated molecules. (a) By processing methods. (b) By electronic function in an OLED. (c) By electronic function in an organic solar cell.

sublimation temperature below the decomposition temperature, however, defines an upper bound for the molecular weight, implying that long oligomer and polymer chains cannot be evaporated.

The function a molecule performs in a device structure depends largely on its absorption or emission energy and on the energy of the molecular orbitals relative to the electrode workfunctions or relative to other molecular materials used. In general, it is nearly impossible to chemically optimize the energy levels in a molecule such that it is at the same time well suited to transport positive and negative charges, emit light, and absorb light efficiently in the desired wavelength range. Instead, it is common practice to prepare molecules that are particularly suited to one of these tasks. Thus, molecules that have a high quantum yield of luminescence may be employed as efficient emitters in OLEDs, and those with a high absorption cross section at the wavelength of interest are used as absorbers (or "light-harvesting molecules") in solar cell structures. Molecules that readily give up electrons may be well suited to transport holes and are thus referred to as *hole-transporting molecules*, while the converse is the case for *electron-transporting or electron-accepting molecules*. A few examples of commonly used compounds can be found in Figure 1.5.

A further distinction is whether the molecule contains only nonmetals or also metals. Organic molecules contain no metals. If the molecule entails a bond between a carbon atom and a metal, it is referred to as *organometallic*. Figure 1.5a shows typical organometallic molecules, i.e. some *coordination complexes*. There, a metal forms the coordination center that binds to organic moieties, the *ligands*, by a *coordination bond*. The coordination bond is also referred to as a *dative bond* because both shared electrons forming the bond are provided by only one of the partners. The number of coordination bonds formed is the coordination number, typically 4 or 6. For example, the Ir-complex shown in Figure 1.5 has six coordination bonds that form the corners of an octaeder with the Ir in the center. Complexes made with Pt(II) (see Appendix) form four coordination bonds that lie in a plane (square planar geometry). This is illustrated and detailed further in Box 2.6 in Chapter 2. By the way, if no coordination bond is formed to a carbon atom, yet only to heteroatoms, chemists may speak of a *metalorganic* compound. Depending on whether one, two, three, or more atoms of the ligand bind to the central metal, the ligand is called *monodentate, bidentate, tridentate*, and so on.

Organometallic compounds play an important role in the field of organic semiconductors because they can be phosphorescent and thus allow for the fabrication of highly efficient OLEDs, as detailed in Chapter 3. Since their emission properties depend on their chemical structure, it is useful to be aware of some terminologies used to describe them. For example, if all ligands are identical, the complex is called *homoleptic*, while the term *heteroleptic* is used to denote a complex with different ligands. Sometimes, a ligand is only added to the complex because it helps the chemical reaction, e.g. by increasing solubility. Such ligands are referred to as *ancillary ligands*. Even though ancillary ligands are not meant to significantly influence the electronic properties of the complex, they can nevertheless affect the efficiency and color of its emission [40]. Often, the emission properties are also affected by the way how the ligands are arranged around the coordination center. For example, as just said, the ligands of $\mathrm{Ir(ppy)_3}$ form an octahedron structure (Figure 1.5a). If identical binding atoms of the ligands are arranged to lie in the middle plane of the octahedron together with the central metal, the structure is referred to as *meridional* (*mer*), while the term *facial* (*fac*) is used to denote the arrangement where identical binding atoms form a face of the octahedron (Figure B2.6.1 in Chapter 2). It turns out that the photoluminescence quantum yield of *fac*-$\mathrm{Ir(ppy)_3}$ is about 10 times higher than that of *mer*-$\mathrm{Ir(ppy)_3}$ because in the latter, the nonradiative decay is increased by about a factor of 10. This is related to the difference in bond length in the mer and fac isomers [41].

1.2.3 Polymer Films

The name polymer is composed of the Greek words πολυ and μεροσ, meaning "many" and "part," respectively. It implies that a polymer is a macromolecule that is composed of many repeating single units, the monomer units. In the context of organic semiconductors, "many" usually means at least 100 repeat units (corresponding to a molecular weight of 20 000 Da for the polymer P3HT) because above that value, the optoelectronic and mechanical properties of a polymer film no longer depend on the polymer length. For short chains, the lengths affect the backbone conformation, and hence its intramolecular and intermolecular interactions. Longer chains, however, entangle above a certain threshold value, and the resulting film morphology becomes independent of the chain length [42]. Commercially available semiconducting polymers such as PPV derivatives and polyfluorenes are offered with molecular weight in the range of 50 000 to 100 000 Da, implying they contain about 200–400 repeat units (see Box 1.1). Any chain made with up to 20 repeat units is referred to as an oligomer (ολιγοσ = a few). Molecules containing between 20 and 100 repeat units may be called either a long oligomer or a short polymer, depending on which aspect the author wishes to emphasize.

Box 1.1 Average Molecular Weights of Polymers

When polymers are synthesized, they will not have exactly the same number of repeat units. Instead, there will be a distribution of polymer sizes, with some short chains, many medium-sized chains, and few long chains. A polymer sample can then be characterized by the average weight of the polymer and the width of the associated weight distribution. There are several ways to obtain an average weight, the most important being the *number-average molecular weight* $\overline{M_\mathrm{n}}$ and the *weight-average molecular weight* $\overline{M_\mathrm{w}}$. In general, any average $\bar{x}$ for a quantity with a distribution of values x_i is given by the sum of all values times the probability p_i of it occurring, i.e. $\bar{x} = \sum_i p_i x_i$.

If the probability of a molecular mass M_i occurring in a distribution is considered proportional to the number-fraction of molecules with that mass, we have $p_i = N_i / \sum_j N_j$, where N_i is the number of molecules with mass M_i. This gives you a number-average as

$$\overline{M_\mathrm{n}} = \sum_i p_i M_i = \sum_i \left(\frac{N_i}{\sum_j N_j} \right) M_i = \frac{\sum_i N_i M_i}{\sum_j N_j} \tag{B1.1.1}$$

This is just the arithmetic mean value. If one considers the probability of a molecular mass M_i occurring to be proportional to the weight-fraction of molecules with that mass, one needs to take $p_i = N_i M_i / \sum_j N_j M_j$. This yields the weight-average as

$$\overline{M_\mathrm{w}} = \sum_i p_i M_i = \sum_i \left(\frac{N_i M_i}{\sum_j N_j M_j} \right) M_i = \frac{\sum_i N_i {M_i}^2}{\sum_j N_j M_j} \tag{B1.1.2}$$

In most cases, the weight-average molecular weight is more suitable to characterize the weight of a distribution. This can be seen in the following example. Consider a sample that contains 9 mol of polymers with a molecular weight of 10 000 Da and 5 mol of polymers with a molecular weight of 50 000 Da. (The abbreviation Da stands for Dalton, a synonym for atomic mass unit u. It corresponds to 1/12th of the mass of an isolated ^{12}C-atom, i.e. 1 Da = 1 u = 1.66×10^{-27} kg.) We find

$$\begin{aligned} \overline{M_\mathrm{n}} &= \frac{(9 * 10.000\ \mathrm{Da}) + (5 * 50.000\ \mathrm{Da})}{9 + 5} \\ &= 24\,286\ \mathrm{Da} \cong 24\ \mathrm{kDa} \end{aligned}$$

and

$$\begin{aligned} \overline{M_\mathrm{w}} &= \frac{9 * (10.000\ \mathrm{Da})^2 + 5 * (50.000\ \mathrm{Da})^2}{(9 * 10.000\ \mathrm{Da}) + (5 * 50.000\ \mathrm{Da})} \\ &= 39\,412\ \mathrm{Da} \cong 39\ \mathrm{kDa} \end{aligned}$$

Since the sample contains 250 000 Da of polymers with a weight of 50 000 Da and only 90 000 Da of polymers with a molecular weight of 10 000 Da, the weight-average molecular weight of about 39 kDa seems more representative for the bulk of the material than the number-average of about 24 kDa. As an example, the distribution of molecular mass measured by gel permeation chromatography for the polymer MEH-PPV is shown in Figure B1.1.1, along with the values for $\overline{M_\mathrm{n}}$ and $\overline{M_\mathrm{w}}$.

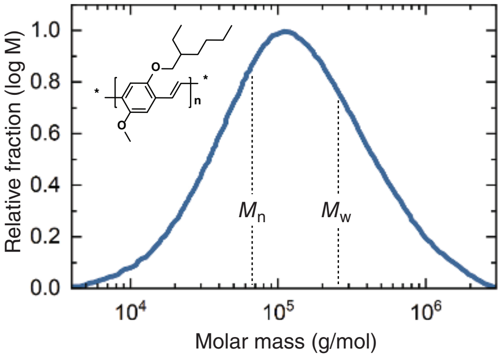

Figure B1.1.1 The distribution of molecular mass for a sample of the polymer MEH-PPV (structure shown as inset). The weight-average molecular weight $\overline{M_\mathrm{w}}$ of 234 000 and the number-average molecular weight $\overline{M_\mathrm{n}}$ of 64 500 are indicated.

The spread of the distribution can be indicated by the *dispersity index Đ* (sometimes still called *polydispersity index [PDI]*), defined as the ratio between the weight-average and the number-average, as follows:

$$Đ = \frac{\overline{M_\mathrm{w}}}{\overline{M_\mathrm{n}}} \tag{B1.1.3}$$

For the example here, $Đ = 39/24 = 1.62$. Often, one is interested in the number *n* of repeat units an average polymer chain contains. This is also called the *degree of polymerization (DP)* (also abbreviated as X). It can be obtained by dividing the (weight-) average molecular weight of the polymer chain by the calculated weight of a single repeat unit.