Chapter 9

ORGANIC SEMICONDUCTORS

One of the most exciting opportunities in optoelectronics currently is devices based on organic materials. These have many advantages, primarily: lower-technology processing with less sensitivity to processing environment (but many are very air sensitive), flexibility, and the opportunity to apply the enormous power of organic synthesis to tailoring the properties of the materials to specific applications. Furthermore, organics can emit light directly as do conventional cathode-ray-tubes and plasma display panels, rather than relying on back-lighting systems such as are used in liquid-crystal displays. One can imagine these technologies leading to poster-sized televisions which can be rolled up and stored in mailing tubes, or unrolled and thumb-tacked to a wall. The materials are already being applied in compact lightweight, power-efficient light emitting devices in small areas such as cell-phone displays. The primary problem with all organic devices is stability. When carriers are injected into these materials, sometimes a molecule falls apart. This does not need to be very common for the device to degrade significantly over relatively short operating times. This chapter considers the options for organic semiconductors and how they are applied.

9.1 MATERIALS OVERVIEW

Organic materials used as active layers in optoelectronics can be divided into two major classes, molecular and polymeric. Molecular organic electronic materials are relatively small molecules, typically with a non-repeating structure – in other words, they are monomers. Details are given in Section 9.1.2. Polymer organic electronic materials, as with other polymers, consist of linked chains of single monomers (simple polymers) or strings of two or more monomers (copolymers). All electronic organic materials, whether monomer or polymer, contain a backbone of "conjugated" bonds, as described in detail in the next section. This structure is essential to achieving conductivity in the molecule. In general, polymers are more soluble than small molecules in common solvents (such as the polychlorinated methanes and tetrahydrofuran [THF]). Thus, polymers are often deposited by spin-coating from a solution, while small molecules are generally evaporated in vacuum. The possibility of functionalizing monomer units or copolymerizing from different monomers allows a single polymer to combine properties of various monomer materials. To achieve the same effect in small molecule structures, several must be co-deposited or otherwise mixed. Likewise, the possibility of producing branched, cross-linked, or network polymers allows greater tailoring of the mechanical properties and greater control of the tendency to crystallize. Both polymer and molecular devices often contain multiple layers to optimize carrier injection into the device and to control the efficiency of recombination of carriers resulting in optical emission. A further advantage of polymers is that thinner active layers may be produced without pinholes and other defects typical in evaporated small molecule films. This can allow operation of a device at lower voltages with the same resulting field. In the following sections, we will consider the structure of selected molecular and polymeric electronic materials. Following this is an overview of typical organic devices. The remainder of the chapter then considers associated issues such as contact materials, and ways of improving the performance of the devices.

9.1.1 Conjugated organic materials

The basic structure of a conducting or semiconducting organic material is shown in Figure 9.1. The essential feature is a continuous series of double bonds that runs the length of the molecule. Molecules with this structure are known as "conjugated". Note that each C atom in the backbone has one bond to each of its neighbors and one bond forming the double-bonded backbone. Because each C atom supplies one bond to this double bonding structure, one of the two adjacent bonds, on average, is a double bond, while the other is a single bond. It does not matter, in principle, which is the double bond and which the single bond. Another way to look at the situation is that each C atom has a half-filled p state available for π bonding, thus the double bonds can be represented as a π-bonded molecular orbital running down the length of the carbon backbone (see below for more discussion). Note that each C atom also has one bond left over for attachment of functional groups, usually a H atom. This opportunity to add functional groups makes conjugated polymers highly adjustable.

The molecular orbital structure of a portion of a trans polyacetylene molecule (Figure 9.1) is shown in Figure 9.2. The carbon atom bonding is hybridized as was discussed for semiconductors in Chapters 2 and 5, with $s+p_x+p_y$ atomic orbitals (Figure 9.2b) forming the sp^2 triangular planar molecular orbital structure and

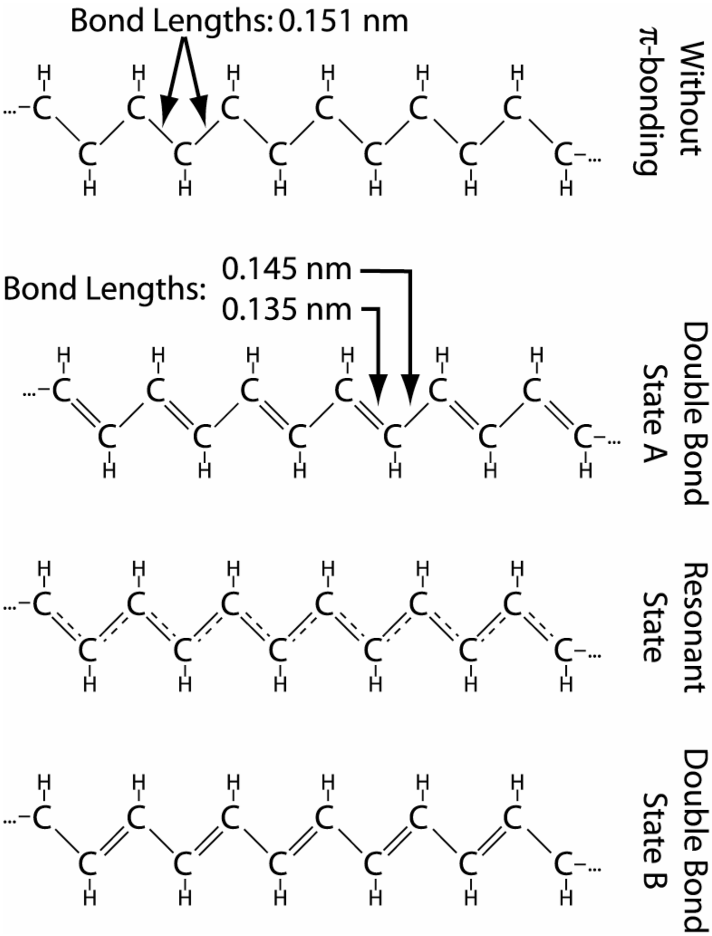

Figure 9.1: A schematic diagram of the simplest fully-conjugated polymer molecule, trans polyacetylene. Three possible configurations are shown for this molecule. In addition, the structure of the molecule in the absence of π-bonding is shown at the top, giving a comparison of bond lengths.

leaving a lone unhybridized p_z orbital projecting along the orthogonal z-axis. The sp^2 hybrid orbitals form conventional σ bonds (Figure 9.2c). (Recall that the bond axis lies along the bond direction in a σ bond.) These bonds have fully paired electrons in their bonding states and empty antibonding states, resulting in a very strong and stable covalently-bonded molecular backbone. The unhybridized, half-filled p_z orbitals form the π bonds (Figs 9.2c and d). (Recall that in π bonds the bond axis is perpendicular to the bond direction.) The energy of the resulting molecular orbitals

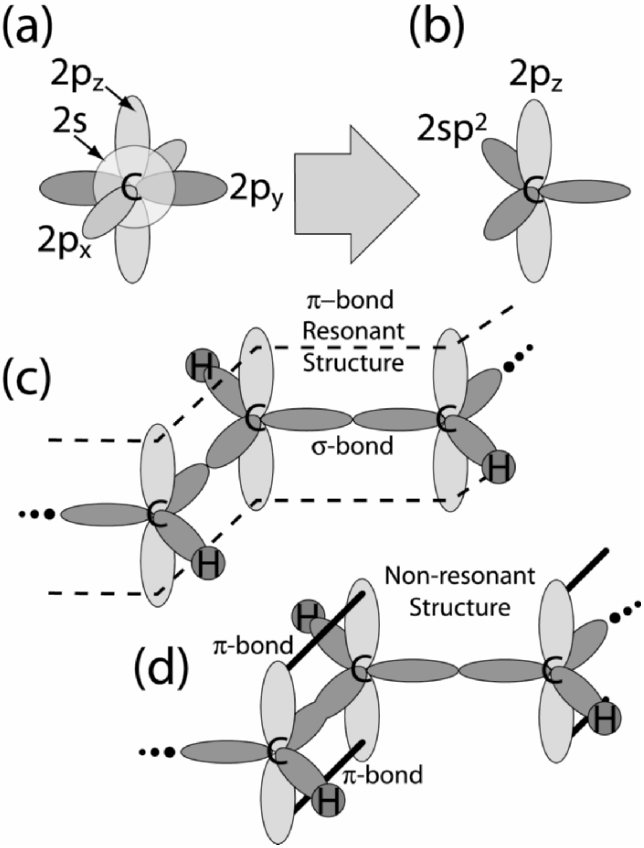

Figure 9.2: A schematic of the hybridization and bonding in poly-ene structures. (a) shows the valence atomic orbitals of C, (b) the hybrid molecular orbitals in poly-enes, (c) the resonant backbone structure of a poly-ene, and (d) the structure resulting from the choice of one of the two possible double bonding structures.

and the filling of these states with electrons is shown schematically in Figure 9.3 for octatetraene (polyacetylene with only 8 C atoms in the backbone).

Adding more C atoms results in more states near both the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) states shown. Because each C atom brings in, on average, half filled states, the molecular structure fills all of the orbitals for which bonding dominates without filling any of the orbitals with primarily antibonding character as in other semiconductors. Thus, the bonds are very strong. Furthermore, because the π bond is specific to a particular direction, the double bond is rigid and the molecule is not free to rotate the bond. This leads to rod-like molecular structures. In contrast, flexible molecules have single-bonded backbones such as in polyethylene. (Single bonds are free to rotate around their bond axes.) As with inorganic semiconductors, there is an energy gap between the HOMO and LUMO states. It is this gap that makes most polymers (conjugated or not) insulating or semiconducting.

The situation in trans polyacetylene, and in other linear trans poly-ene's is, unfortunately, more complicated than the picture represented by Figure 9.1 would suggest. The simple symmetric structure with a π-bonded backbone (Figure 9.2c) (determined from a Hückel calculation for example), does not account for electron correlation effects. With correlated electron motions, each electron interacts with all other electrons rather than behaving as if it were the only electron present. Electron-electron correlations alter the state energies and exchange one state with another as, for example, the LUMO. This is unfortunate because the LUMO is transformed from a symmetry different from that of the HOMO to the same in most cases. This simple

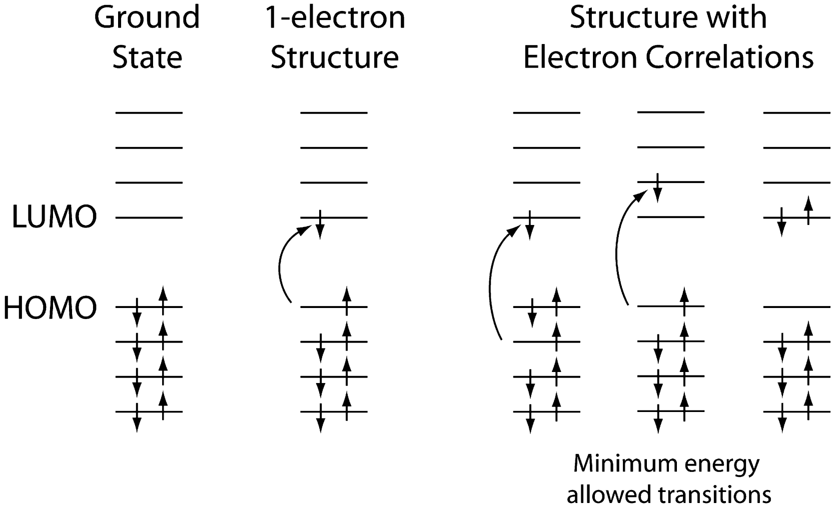

Figure 9.3: Shows the molecular orbitals for trans octatetraene ignoring, hydrogen-carbon bonds, and the filling of these orbitals with electrons. Both possible transitions that would result from a 1-electron model of the structure and the actual result including electron correlation effects are also shown, indicating that the lowest energy optical transitions are not from the HOMO to the LUMO states. Only a two-electron transition is allowed between these states for a photon-only process. Reprinted with permission from Brédas, Jean-Luc et al. "Excited-state electronic structure of conjugated oligomers and polymers: a quantum-chemical approach to optical phenomena". *Accounts in Chemical Research* 1999; 32:267-276. [1] Copyright 1999 American Chemical Society.

statement has profound consequences for an optical material. In a single photon process, quantum mechanical selection rules forbid transitions between states of like symmetry. The electron correlation effect changes the HOMO-LUMO transition from allowed to disallowed. The effect is similar to converting an inorganic semiconductor from direct to indirect. While optically-active transitions still exist within the molecule, they are no longer the lowest energy transitions. Thus, electrons and holes in their lowest-energy states in organic molecules cannot normally recombine radiatively in simple molecules such as trans-polyacetylene, see Figure 9.3.

Repeating this important point, it is possible for organic molecules to behave as do *indirect-gap* semiconductors, reducing the light emission probability.

In addition to electron correlation effects, there are structural asymmetries that must be considered. As mentioned above, in a simple molecule such as the trans polyacetylene the structure has exactly one double bond per two bonds along the chain. In a perfectly symmetric structure, either of these bonds could be the double bond or the structure could resonate (Figure 9.1), switching the double bond from one side to the other so fast as to be indistinguishable. However, the electron density in a double bond is higher than in a single bond and the consequent bond length is smaller. Thus, picking one of the double-bonding states of the molecule (state A or B in Figure 9.1) defines a short double bond. This, in turn, specifies that the next bond should be longer, the following bond shorter, and so on down the molecular backbone. It further turns out that the non-resonant states have lower energies than the resonant state (shorter overall bond lengths in the non-resonant state). In the resonant state the molecule is completely symmetric and would be a metal with the HOMO and LUMO at the same energy. Breaking the resonance to choose a specific double-bond pairing leads directly to the HOMO/LUMO gap. This stabilization has important consequences for the behavior of the molecule, as we shall see below.

The symmetry breaking of the bond lengths also applies to more complex molecules such as poly-paraphenylene vinylene (PPV). The three possible double bond configurations of this molecule are shown schematically in Figure 9.4.a-c.

One of the most important concepts in π-bonded molecular orbital (MO) structures is that of nodes. MOs are generally understood as being made up of linear combinations of atomic orbitals (AOs), as discussed in earlier chapters. Any such combination will include positive and negative terms. (See, for example, Equations 2.5 and 5.11.) The situation is generally represented schematically as shown in Figure 9.5. Here, a “+” lobe above the molecular backbone represents the opposite sign in the MO sum from terms with a “-” lobe above the molecular backbone. Mathematically and physically, AOs for given atoms being added together in this manner are identical. Thus, the sum of two AO’s gives a high electron density between the atoms (bonding) while a difference of AOs gives a node, resulting in zero electron density at the bond center

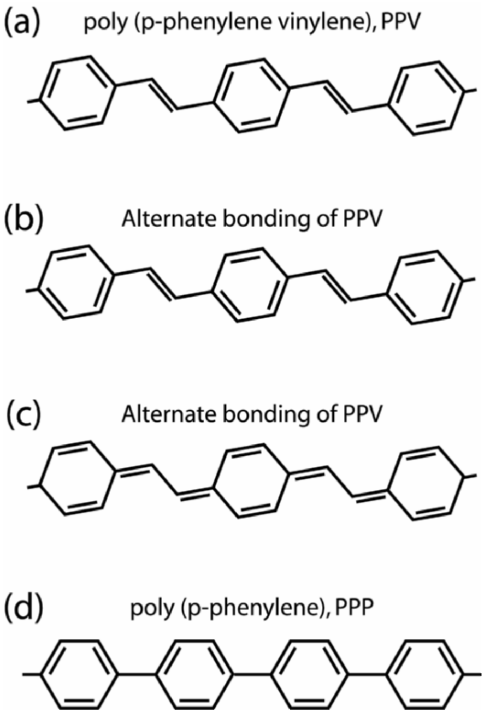

Figure 9.4: Structure and three possible double-bonding arrangements for PPV (a-c) and the structure for PPP (d). Note that PPV structure (c) has a higher energy than structures (a) and (b). Thus, (c) represents an excited state.

(antibonding). For a given combination of AOs there will be a given number of (regularly spaced) nodes.

Each combination of sums and differences of AO's down the π-bonding structure represents one electronic state of the system that can accommodate exactly two electrons. The resulting MOs include both bonding and antibonding character. The overall bonding/antibonding behavior of all but two molecular orbitals is somewhere between a pure bonding state (zero nodes) and a pure antibonding state (one node per bond). In Figure 9.5, the four structures shown are the highest and lowest energy states along with the HOMO and LUMO states for trans polyacetylenes. Notice that these structures are highly symmetric with well defined wave-like alternations of AO sign and regular spacing of nodes. This is because the resulting MOs are wave-like as was the case for Bloch wave states in solids, discussed in the free and nearly free electron models of inorganic semiconductors (Chapter 2). One can see that the energy of an MO increases as the wavelength of the node pattern decreases, exactly as it does with increasing wavevector for free electrons. A striking feature of the MO polarities and nodal wavelengths in the HOMO and LUMO states shown in Figure 9.5 is that the structures are nearly identical. The only difference is that the nodes in the HOMO state are localized on the single bonds of the structure while in the LUMO state the nodes are localized on the double bonds. In other words, the electron density for an electron in the HOMO state is localized on the double bonds while the LUMO electron density is on the single bonds. Consequently shifting an electron from the HOMO to the LUMO state (Figure 9.3) shrinks the single bonds and expands the double bonds.

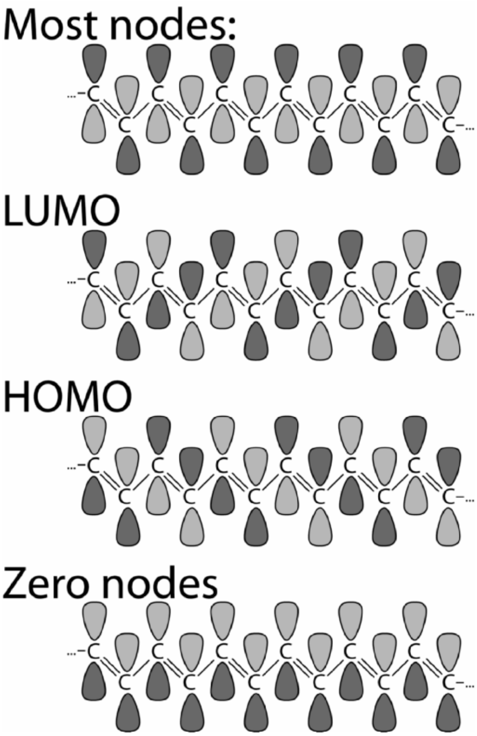

Figure 9.5: The lowest and highest energy nodal structures possible in trans polyacetylene along with the HOMO and LUMO states. The more nodes occur in the structure, the higher the energy of the linear combination of atomic orbitals. The HOMO and LUMO states divide at the point where half of the states have been filled. Thus it is perhaps not surprising that every other bond would have a node at this point. Reprinted with permission from Brédas, Jean-Luc et al. "Excited-state electronic structure of conjugated oligomers and polymers: a quantum-chemical approach to optical phenomena". *Accounts in Chemical Research* 1999; 32:267-276. [1] Copyright 1999 American Chemical Society.

At the same time it increases the electron density on the single bonds and reduces density on the double bonds. This coupling of atomic positions (shifted through atomic vibrational modes or phonons) with electron modes is the same type of coupling that occurs in indirect gap semiconductors. It is immediately evident that molecular design for optical activity will require a minimization of the molecular distortional changes associated with a transition from the HOMO to the LUMO states. In long molecules such as those shown in Figs 9.1 and 9.5, the coherence distance of distortions associated with a charge in an excited state do not propagate over the entire molecule. It is estimated that the excited state affects 2-2.5 nm of the chain. [2] The bond distortion pattern of the excited section is interpolated to the distortion pattern of the unexcited section through a resonant region.

Molecules such as poly (p-phenylene vinylene), Figure 9.4.a, or poly (p-phenylene), Figure 9.4.d, contain more phenyl rings and fewer linear chain segments than trans polyacetylene and similar molecules. The phenyl rings have a weaker distortion pattern and are often considered truly resonant structures. Consequently, there are smaller changes of the structure for HOMO to LUMO transitions, and the optical activity of the molecule is higher. Similar distortion wave phenomena occur in small molecules during excitation. We will see, for example, that the dye molecules discussed in the molecular optoelectronic materials Section 9.2, following, are made up primarily of linked functionalized ring structures rather than π-bonded chains and are highly efficient in radiative exciton recombination.

9.1.2 Ionized organic molecular structures

The above discussion shows that the bonding structure of fully conjugated organic molecules leads to a strongly bonded insulating state, as is the case in cold semiconductors. We are now prepared to consider what a free electron or hole might look like in an organic molecule. A free electron in a semiconductor exists in an antibonding state. Likewise, a free electron in an organic molecule usually occupies the lowest energy predominantly antibonding state (the LUMO). Occupying this state eliminates a double bond (both the bonding and antibonding states are filled on one atom). This leaves a negative charge on one atom and an unpaired electron on the other. The unpaired electron is known as a soliton or a free radical and is typically distributed over a moderate distance (1-2 nm) on the carbon backbone. Likewise, removing an electron (creating a “hole”) removes one of the electrons forming a double bond and breaks the bond, leaving a positive charge behind on one atom and a soliton on the other atom.

Charged states on molecules can also be viewed as the result of oxidation or reduction processes. To see how charge states can be developed by these reactions, consider a misalignment of the double bonds on the backbone of polyacetylene, leading to an unpaired electron, as shown in Figure 9.6a. This soliton or free radical and has no net charge. However, the extra electron (half-filled dangling bond) is highly reactive. Oxidation then can remove this electron, leaving a positive residual charge (Figure 9.6b), while reduction can leave an extra electron behind, pairing the

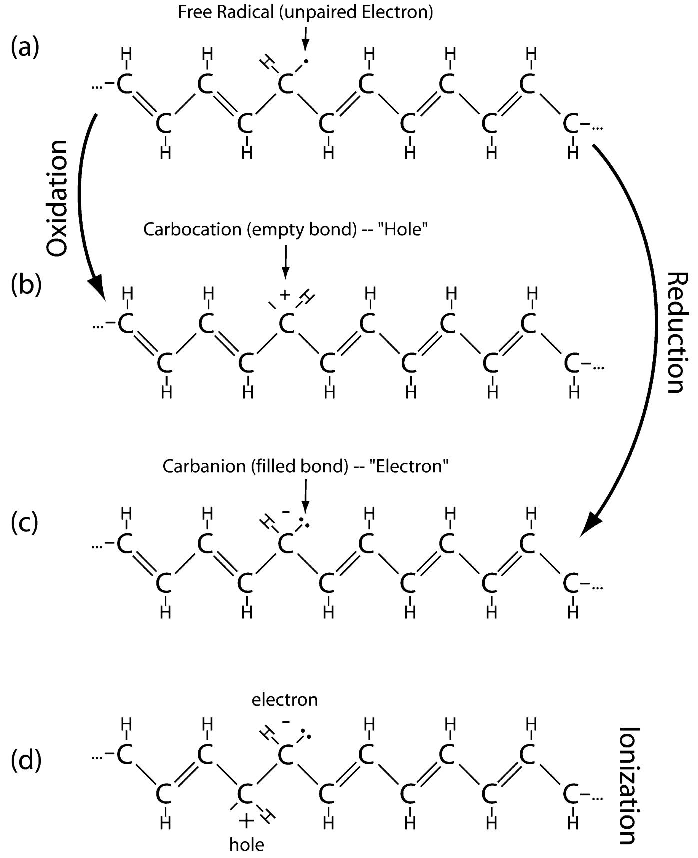

Figure 9.6: Bonding configurations for imperfectly bonded states of trans polyacetylene. (a) Shows the result of a reaction leaving a reduction in conjugation (a mismatch in the double bonding structure, known as a free radical. These are highly reactive sites and not stable in bulk solids. (b) Shows the organic molecule equivalent of a hole in an inorganic material, (c) an electron, and (d) an electron hole pair.

electrons on the dangling bond (Figure 9.6c). These charged defects are free to diffuse along the backbone of the molecule. This process of oxidation or reduction of the backbone is a standard method for achieving conductivity, effectively doping the polymer.

The negatively charged atom (Figure 9.6b) is referred to as a **carbanion**, while the positively-charged atom (Figure 9.6c) is a **carbocation**. Either of these structures (or both) can occur on a conjugated molecular backbone. As one can see by a close examination of the bonding of the molecule, both of these cases break the alternation of the double bonds, leading to a situation in which one atom has an unsatisfied desire to form a double bond. Consequently, the molecule reorganizes its bonding to maximize the number of double bonds on the backbone (Figure 9.6). One can quickly establish however, that in most cases the electron count does not work out. In fact, this will always be the case when one transfers a single carbocation or carbanion from one molecule to another and always creates not only a charged defect but also a soliton. When two defects are present on opposite sides of the molecule the two corresponding solitons can join to reconstitute a double bond on their own leaving a separated carbanion/carbocation pair on the molecule without additional partially filled dangling bonds.

The equivalent of an electron-hole-pair or exciton results from a carbocation lying on a site on the backbone of the molecule adjacent to a carbanion. This would also be the result of breaking a double bond where both electrons of the double bond went to one atom of the double bonded pair, leaving a negative charge on that atom and a positive charge on the other atom (Figure 9.6d). A carbocation-carbanion pair on adjacent C atoms is particularly favorable for two reasons. First, the opposite charges of the carbocation and carbanion experience an electrostatic attraction, as in an exciton in an inorganic semiconductor. Second, the bonding distortion pattern on the nearby π-bonds is less affected than the distortion pattern for separated defects. These contribute to a strong binding of the carbocation to the carbanion. In solar cells and photodetectors where charge separation following light absorption is required, this binding energy reduces the efficiency of current generation and increases the recombination rate. In light-emitting devices, the exciton binding energy coupling the carbocation to the carbanion lowers the energy of the emitted photons relative to the energy of a pair of dissociated defects. Exciton binding energies in organic molecules have been estimated to range from 0.1 eV to as high as 1.0 eV. [1] These very high binding energies have the advantage for light emitters that once an exciton forms, radiative recombination of the charges, reconstituting the double bond, is likely. This tends to reduce loss of free carriers in the thin emissive organic layers and increase their light emission efficiency per unit current injection (see the discussion of light-emitting devices below).

An interesting feature of carbocation/carbanion pairs is that when the charges separate, they remain on the side of the backbone of the carbon chain on which they began. This is the result of the need to maintain the double bonds on the remainder of the structure and the bonding distortions associated with the charged defect. Only when the two are on opposite sides of the molecule can the double bond be reconstituted by transfer of the electron. When the double bond does reform, a large amount of energy is released as an electron is transferred from a filled antibonding state to an empty bonding state. This extra energy can be released as heat or light as for inorganic light emitters. The possibility of light emission is the basis of organic optical devices. The situation described above is summarized schematically in Figure 9.7.

Note that all states in these molecules are resonant states, as with Bloch waves and so are more delocalized than this description suggests.

There is a temptation to discuss organic electronic materials and devices in the same terms as for inorganic materials and devices. Thus, the HOMO state becomes the valence band edge, the LUMO state is the conduction band edge, carbocations become holes and carbanions become electrons. With these substitutions, the discussion in broad terms is identical to that of Chapters 2 and 3. However, this picture is inaccurate and deceptive in a number of ways. Recent calculations, for example those by Köhler and collaborators [3] have shown that molecular orbitals on one carbon atom interact only with the nearest few repeat units on a polymer such as PPV and only weakly from molecule to molecule. Interchain electronic interactions are further complicated by the irregular structure of the organic matrix (although local crystallization of some materials can have a strong influence on this situation).

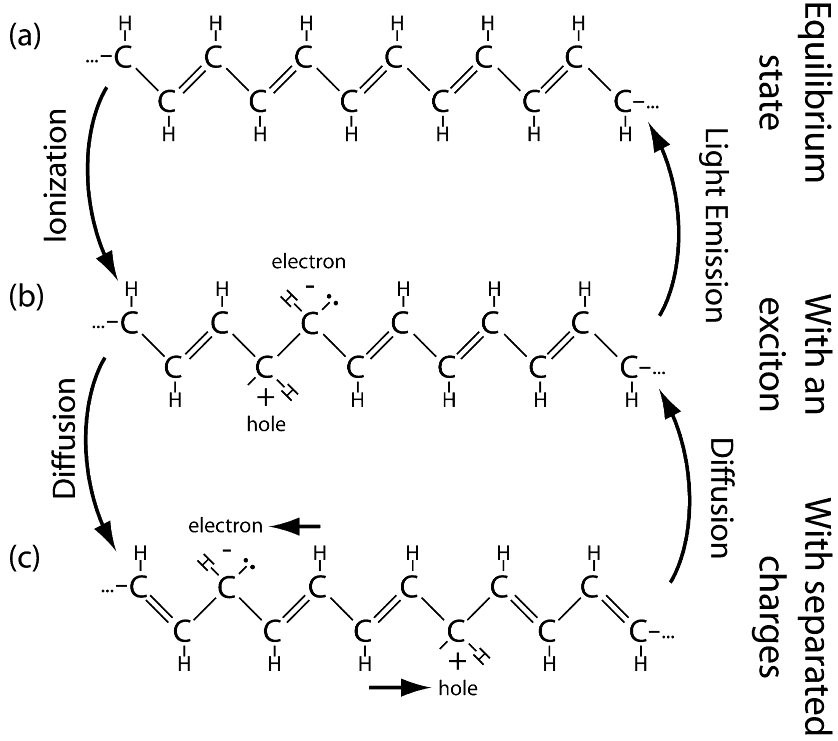

Figure 9.7: Schematic diagrams showing the transition from the equilibrium state of trans polyacetylene to states with an exciton and two separated carbocation and carbanion charges. (a) The equilibrium state, (b) the molecule with a carbocation+carbanion pair bound together as an exciton, and (c) with the two charges separated.

This topic is a matter of intense current research and remains to be fully resolved. Nonetheless, it is clear that the interactions of bonds are weak enough to produce little broadening of the molecular orbitals into bands and little delocalization of the bonding structures. This lack of interaction is, in part, responsible for low carrier mobilities in these materials. Consequently, it is inaccurate to think of organic electronic devices in terms of bands and free carriers and preferable to stick with a more traditional physical chemistry lexicon based on HOMO and LUMO states and localized oxidation and reduction of the bonding structure to produce carbocations and carbanions. One can go too far in this direction as well. Significant broadening in the optical emission properties of organic molecules occurs as one transitions from light emission of single molecules in solution to emission from solids composed of many molecules. This indicates some level of broadening and band formation. Nonetheless, the band-like behavior is much less significant than in inorganic semiconductors and the dominant behaviors are intramolecular rather than intermolecular except in the case of charge transport where interchain transfer is critical. In spite of the admonition above that it is inaccurate to refer to carbanions and carbocations as “electrons” and “holes” in organic materials, the remainder of this chapter will generally use these oversimplified terms for convenience. In most cases, the distinction is not significant.

It is interesting to note that in general the mobility of holes (carbocations) is higher than the moblity of electrons (carbanions) as there is a greater overlap from one molecule to another in the HOMO bonding states than in the LUMO antibonding states. [1] The overlap between molecules is strongest as the distance between the chains shrinks. Unfortunately, this has the simultaneous effect of rehybridizing the bonding structures to increase the energy of the lowest-energy optical transition relative to the HOMO-LUMO gap in some molecules (as was the case in polyacetylene). Consequently, *optical emission is quenched as the distance decreases in some molecules*. This is primarily a problem when the long axes of the molecules lie parallel to one another as in organic crystals. Thus, organic crystals often will give a relatively high carrier mobility and a relatively low luminosity. Such materials are beneficial to organic transistors that rely on high mobility of carriers for improved performance, while amorphous structures provide better performance in optical devices. Indeed, we shall see below that the efficiency of luminescent devices degrades if the organic matrix crystallizes. In spite of these trade-offs, in the some optimal materials, both good mobility and high luminescence (quantum efficiencies approaching one) is obtained. The fact remains though that typically optical luminescence and carrier transport are inversely related.

9.2 OVERVIEW OF ORGANIC DEVICES

Before turning to details of specific organic materials used in devices, it is helpful to examine the typical structure of such devices. Organic devices are similar to conventional devices in some ways but dramatically different in others. Organic materials have exceptionally low carrier mobilities relative to conventional inorganic crystalline materials (and even compared to a-Si:H in many cases). Doping levels are generally relatively low as doping requires oxidation or reduction of the organic material. Thus, many devices, and in particular light-emitting devices, do not have a p-n homojunction nature as in inorganic devices. Rather, they resemble the p-i-n structures in amorphous Si solar cells discussed in Chapter 8. Thus, the built in or applied field generally is dropped across the entire device. In other words, there are no depletion regions – the entire device is a depletion region as in a capacitor. The low carrier mobilities require relatively high fields to obtain adequate current injection and conduction through the organic layer. This is reflected in the relative thinness of the final devices and the high fields at which they often are forced to operate (10^5 V cm^{-1} or more).

9.2.1 Light emitting devices

The basic structure of all organic light-emitting devices (OLEDs) is shown schematically in Figure 9.8. The structures are usually deposited on glass substrates coated with indium-tin oxide (ITO), a transparent conducting oxide, as anode. The active layers consist of one or more polymer or molecular films, generally well below 1 μm in thickness. If a single layer is used, that layer must transport both holes and electrons, accept both efficiently from the contacts, and emit light by carrier recombination. This combination of properties has been difficult to achieve in a single material. Therefore, both polymer and molecular materials adapted to act primarily as electron transport layers (ETLs) or hole transport layers (HTLs) are used. Light emission is usually incorporated into one of these materials either by addition of dye molecules or by design of functional groups and the basic structure of the ETL or HTL itself. Additional layers may also be included to improve carrier injection. In some cases (usually in molecular organic devices) a layer optimized to trap carriers of both types and promote radiative recombination is included. Finally, the device is completed by deposition of a cathode metal, which is responsible for electron injection into the ETL. The anode is usually incorporated into the substrate. Specific materials used for many of these layers and issues associated with them are discussed in later sections. Additional details may be found in the literature.

The emission intensity from current devices similar to the one illustrated in Figure 9.8 deteriorates with time. The absolute efficiency of the device (optical power out per Watt of input power) also varies significantly from device to device. The major factors limiting the performance of an organic light-emitting diode (OLED) have been discussed in detail by Patel et al.. [4] The four primary limitations to total optical emission intensity are as follows.

(1) An imbalance in the carbocation and carbanion injection rates on the two sides of the device. This causes net transport of one type of carrier completely through the structure to the other electrode. This is inefficient, as the transported current generates no light. It results from dramatic differences in the electrical properties of the two contacts and the absence of adequate barriers to transport of either or both types of carrier through the entire device.

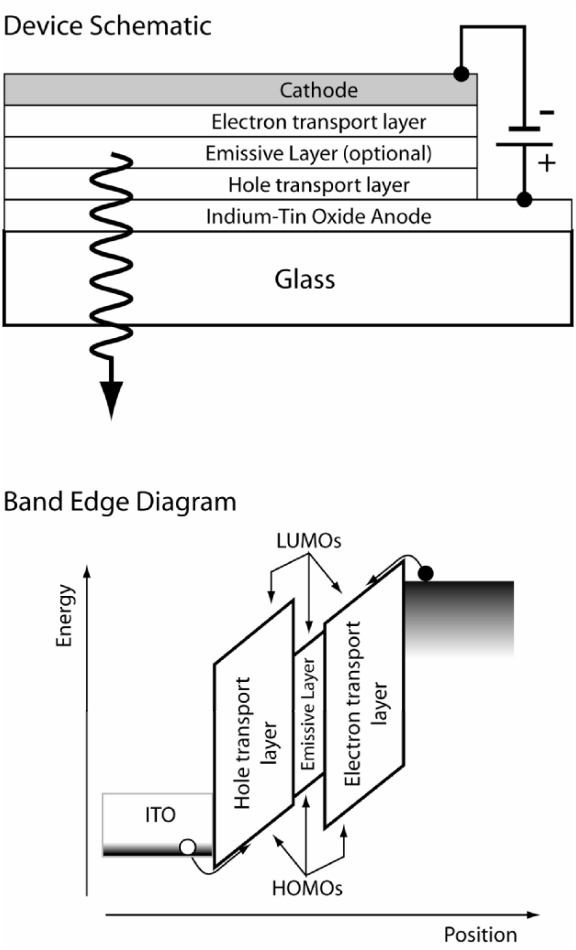

Figure 9.8: A schematic diagram of a typical organic light-emitting device along with a band-edge diagram for the device under forward bias (for light emission). The hole transport layer (HTL) has a relatively high HOMO energy and accepts and transports carbocations relatively easily. A potential barrier between the HTL (or emissive layer) and the electron transport layer (ETL) blocks further transport of the holes. Likewise, the ETL accepts and transports carbanions relatively easily. Emitted light escapes through the indium tin oxide (ITO) anode and the glass.

(2) The electronic state distribution of the excitons trapped in the material affect recombination efficiency. An excited configuration of a molecule consists of an excited electron in a LUMO state paired with a hole in a HOMO state. The hole,

however, is the absence of an electron in a state that normally holds two electrons. Thus, effectively, the high-energy electron must mesh well with the electron in the half-filled HOMO into which it would fall. In order that the high-energy electron can relax into a low-energy state, it must have the opposite spin from the other electron in the low-energy state and the spins of the two electrons must precess with opposite phase. There are four possible arrangements of spin and phase, (see Figure 9.9) but only one of these allows recombination (opposite spin and phase). Thus, recombination is allowed for one (singlet) state and disallowed for three (triplet) states. The relative populations of carbocation/carbanion pairs in the singlet and the three triplet states controls the recombination rate. Unfortunately, in some organic materials, electron correlation effects stabilize the triplet states relative to the singlet states, reducing the efficiency of radiative recombination.

The solution to this is to add molecules incorporating high mass metals such as rare earths. These elements assist in flipping the electron spin and phase in the triplet state, transferring the exciton to the singlet arrangement, allowing recombination and greatly increasing radiative efficiency. Dye and spin-mediating molecules and their design are discussed briefly below. In long-chain molecules the situation is softened somewhat, resulting in a higher population of singlet states (the energy of the singlet is reduced in the polymer), although the mechanism is not known.

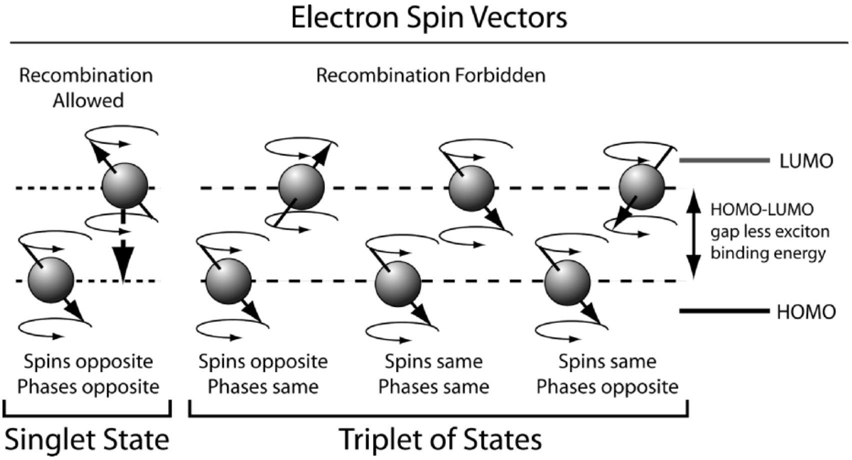

Figure 9.9: A schematic representation of the various relative wave function relationships between electrons in a bound exciton. Only when the electrons have opposite spin and opposite precession phase can recombination occur based on quantum mechanical selection rules.

(3) The efficiency of radiative recombination decay of the singlet state as compared to possible non-radiative processes controls luminescence efficiency. The most common reason for lowering of the radiative recombination rate is diffusion of impurities into the organic layer, usually from the contacts. Recombination of excitons at a contact also lowers efficiency. Increasing the organic layer thickness and providing barriers to excitons diffusing to the contacts can improve this.

(4) Escape of light from the device is required for it to be useful. Light is given off isotropically in most cases but it escapes only through the transparent front contact. Inward-directed light must be reflected toward the transparent contact. At the same time, light moving outward must not be reflected back into the device at interfaces. Reflection can be reduced by standard optical film techniques such as by use of anti-reflection coatings. Reflection from the back of the device may be enhanced by choice of the back contact metal.

Resulting devices have achieved relatively good performances in a startlingly short time. An illustrative comparison of device performances is given in Figure 9.10 (after Roitman et al.). Recent results continue to increase efficiencies, luminosities, and lifetimes, although the rate of further increase is slow. In some cases, internal quantum efficiencies have approached 100% (all injected current results in photon generation). However, this efficiency generally decreases dramatically as power levels are increased where more non-radiative processes become active. Furthermore, the performance of devices generally degrades with time.

The degradation rate increases as the device is driven harder. Thus, the higher the current injected into the device, the shorter its lifetime. Lifetimes also vary depending upon the wavelength of operation and the contacts and other materials used. These effects are discussed in detail below.

9.2.2 Transistors

Field effect transistors have been demonstrated based on both molecular and polymer organic semiconducting materials. [See References 5 and 6, respectively, for examples of these devices] A typical device, such as that illustrated in Figure 9.11 consists of an organic semiconductor coated onto a dielectric such as SiO_2 and making use of an underlying gate electrode for conductivity control. Source and drain contacts underlie the edges of the organic channel, as shown in the figure. Carrier mobilities in molecular organic TFTs exceeding 2 $cm^2\ V^{-1}s^{-1}$ with on/off current ratios in excess of 10^8 have been achieved. In the device reported by Jackson et al., [5] the organic semiconductor was pentacene (see Section 9.3, below).

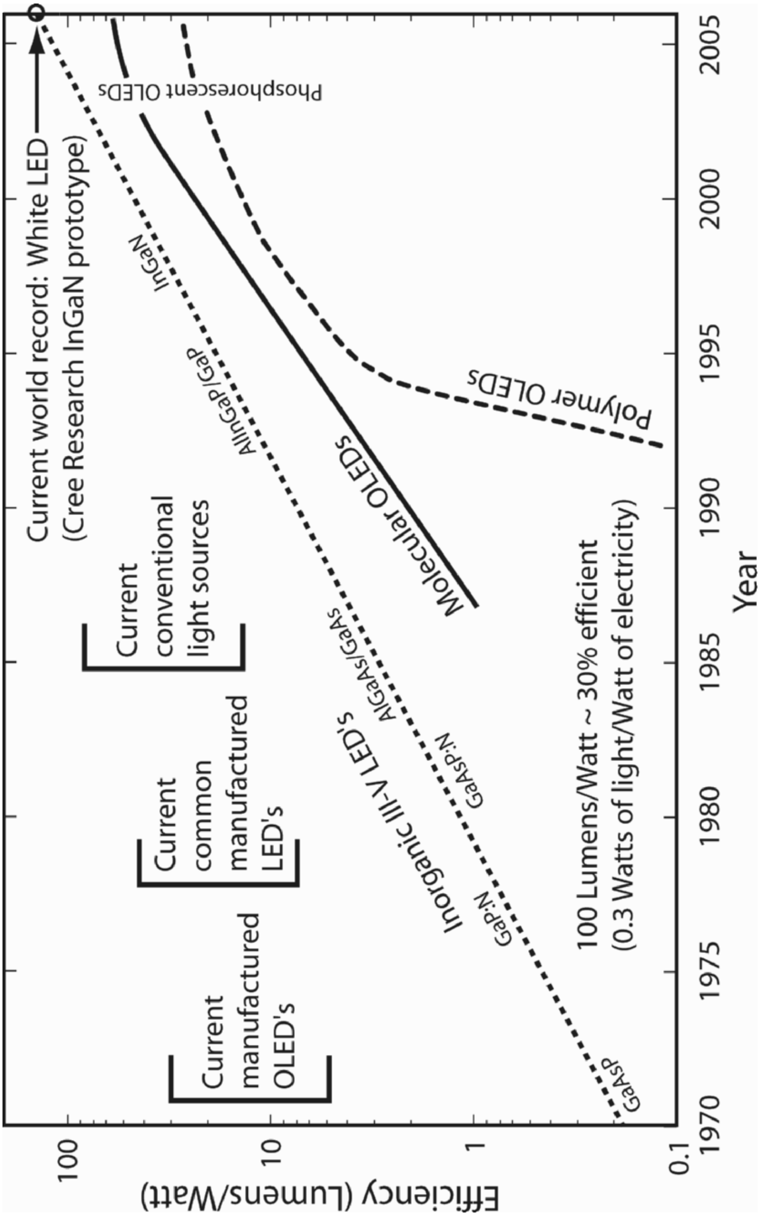

Figure 9.10: Efficiency of solid-state light emitters as a function of time. Ranges for current commercial devices are also shown. Data based on references 2-4 in Chapter 1.

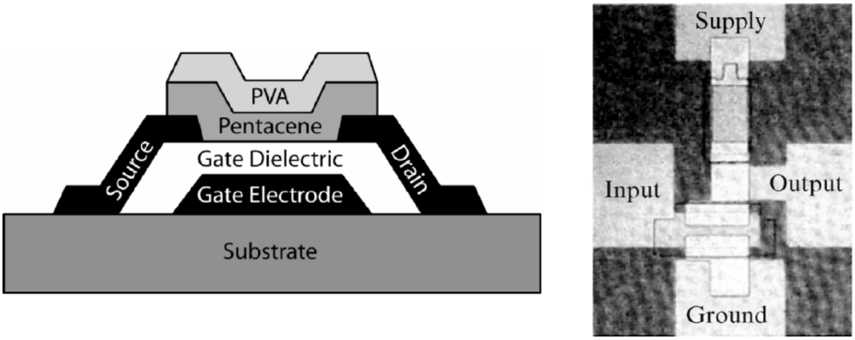

Figure 9.11: A schematic diagram of the elements and structure of an organic TFT (left) along with an image of an actual device. The PVA serves to encapsulate the device. With permission from: Jackson, T.N.; Lin, Y-Y.; Gundlach, David J.; and Klauk, H.; “Organic thin-film transistors for organic light-emitting flat-panel display backplanes.” *IEEE J. Sel. Topics In Quantum Electronics* 1998; 4: 100-4. Copyright [1998] IEEE.

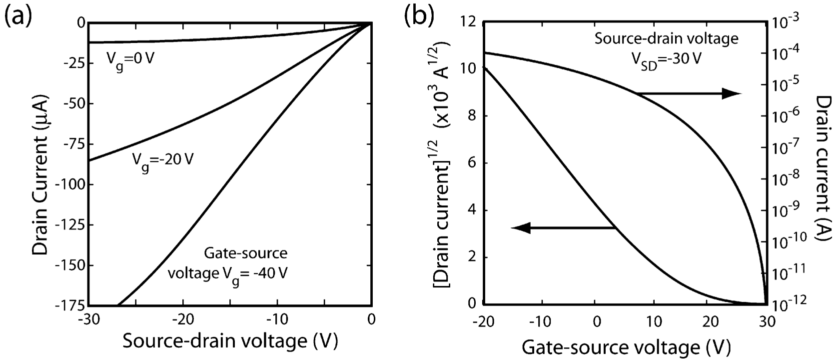

Figure 9.12: Device characteristics for a pentacene TFT. With permission from: Jackson, Thomas N.; “Organic thin film transistors-electronics anywhere” *Proceedings of the 2001 International Semiconductor Device Research Symposium*. Copyright [2001] IEEE.

To achieve high carrier mobilities, highly organized molecular or polymer layers are necessary as chain-to-chain or molecule-to-molecule charge transfer generally limits the mobility. High levels of crystallinity assist such transfers. Remember that this is the opposite of the case for organic luminescent materials where an amorphous structure is preferred. Treatment of the substrate and careful control of the deposition conditions are generally necessary to obtain the highest crystallinity. In addition, very regular molecules such as pentacene are needed for such layers. An example of the current/voltage characteristics of a typical resulting TFT is shown in Figure 9.12.

One of the complications in fabrication of organic electronic devices is patterning of layers. In standard microelectronic processes, application of a polymer photoresist, exposure and development of the resist, etching of the layer to be patterned, and removal of the resist are used to pattern a layer. The problem in organic devices is that the layer to be patterned is essentially the same material as the resist itself. Thus, any method of removing the resist tends to remove the organic layer as well. Consequently, patterning has been primarily accomplished through printing (using ink-jets or other methods) or by evaporation through a shadow mask. This limits the size of the devices and the possible processing steps used.

The devices described above have rather high gate voltages. These can be reduced significantly by using higher dielectric-constant gate insulator materials such as barium zirconate titanate. For an example, see Dimitrakopoulos et al. [8]

9.3 MOLECULAR OPTOELECTRONIC MATERIALS

As noted at above, organic semiconductors can be divided into two major classes of materials, small molecules and polymers. This section reviews some of the more common small molecules currently used in organic electronics. The following section considers the polymers.

The small molecular organic semiconductors typically consist of phenyl or napthyl groups coupled together. The electronic structures of these molecules differ from one molecule to another in the coupling of HOMO and LUMO states within the molecule and from molecule to molecule. The differences provide relatively good conduction for either carbanions or carbocations. Thus the molecules are often described as electron (ETL) or hole (HTL) transmitting layers, respectively. In general, hole transmitters have relatively high HOMO energies while electron transmitters have relatively low LUMO energies. More importantly, carbocations ("holes") are distributed broadly across the molecule in HTL's while carbanions ("electrons") are localized. The converse is true in most ETL's. The most common electron transmitter is tris-(8-hydroxyquinoline) aluminum (Alq_3). There are a variety of hole transmitters with generally similar structures. A typical example is *N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine* (NPD). The structures of these molecules are discussed in detail in the following Sections, 9.3.1 for ETL's and 9.3.2 for HTL's. These two molecules are used commonly in light emitting devices. In general, a different set of molecules is used for switching devices (FET's for example), which are optimized for carrier mobility and conduction properties at the expense of light emission. Two of the more popular small molecules in current use for transistors are pentacene and α-sexithienyl. These are considered in detail in Section 9.3.4. Finally, in light-emitting devices small dye molecules optimized for radiative recombination of carbocations and carbanions are added to enhance efficiency as discussed in Section 9.3.3.

Molecular organic semiconductors are generally deposited by vacuum evaporation as they are typically insoluble and thus difficult to spin-cast or ink-jet print, but are stable and have reasonable vapor pressures and are therefore evaporable. Vacuum evaporation is more complex than spin-casting but provides quite pure materials with well-controlled structure and layer thickness. It is also straightforward to produce multilayer structures by evaporation.

9.3.1 Molecular electron transporters

The near ubiquitous choice for the electron transporter molecule in OLEDs and related devices is tris-(8-hydroxyquinoline) aluminum (Alq$_3$), shown in Figure 9.13. This molecule has proven highly reliable and durable and is nearly always used in contact with the cathode. Alq$_3$ has been found to be the most stable electron transporter molecule in conjunction with the low-work-function cathode metals

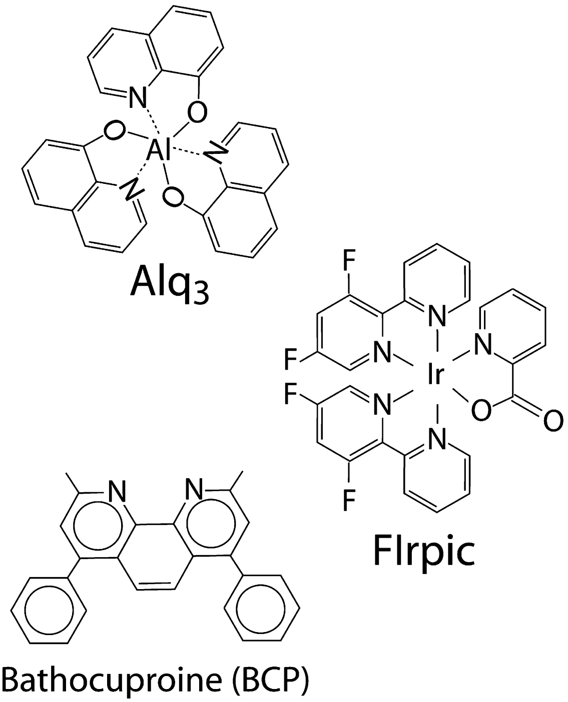

Figure 9.13: The molecular structure of three successful ETLs. Tris-(8-hydroxyquinoline) aluminum (Alq$_3$) is the most common electron transporter molecule in organic electronics and is used in contact with the cathode metal in most devices. BCP and FIrpic are ETLs that provide a barrier to hole and exciton transfer from the anode side of the device into the Alq$_3$.

(including such reactive species as Al and Li) and is relatively resistant to chemical attack. Furthermore, the substantial energy of the HOMO and LUMO states compared to the vacuum level makes electron injection into Alq_3 relatively easy. Other molecular electron transporters have been developed for specific purposes (mostly as hole transport barriers) but are generally used in conjunction with Alq_3 at the cathode.

Numerous theoretical studies have considered the electronic structure of the Alq_3 molecule. See, for example, Zhang and Lee. [9] Calculations suggest that electrons added to Alq_3 molecules are relatively delocalized, and are primarily found on the O, N and Al atoms. The distribution of the charge across the center of the molecule contributes to the high electron mobility. Furthermore, the electronic structure of the Alq_3 molecule is largely unchanged by adding an electron to the LUMO state. By contrast, adding a positive charge to the HOMO results in significant alterations in bonding and the positively-charged state is relatively localized on one of the quinoline units. [9] *This suggests that the mobility of holes will be lower than that for the more generally-distributed electrons and explains why* Alq_3 *is not a good hole transporting material.*

Several other ETLs are used, primarily to block holes injected from the anode from passing through devices. Two of these, 2,9-dimethyl 4,7-diphenyl 1,10 phenanthroline (also known as bathocuproine or BCP) [10] and (bis(2-(4,6-difluorophenyl)pyridyl-N,C2')iridium(III) picolinate) or FIrpic [11] are shown in Figure 9.13. These molecules are primarily designed to have a LUMO state energy similar to that of Alq_3 but to have a larger HOMO/LUMO energy gap. Note how FIrpic has a central structure similar to Alq_3. The distinction between BCP and FIrpic is the ability of the hole barrier to block triplet-state excitons. FIrpic is specifically designed for this purpose and has been shown to provide improved device performance as a result. [11] The range of materials which have been considered as ETL's includes even carbon nanotubes and carbon nitrides. However, the materials listed above are the most successful.

In summary, the most important properties of ETL's, generally achieved in the above materials are as follows. (1) A good energy match between the LUMO of the ETL and the cathode Fermi energy is designed to provide a low barrier to electron injection. (2) A high barrier to holes entering the HOMO states or excitons diffusing from the anode side of the device blocks hole loss to the cathode. (3) A distributed density of negative charge with little change in bonding structure when the molecule contains an extra electron enhances electron mobility. (4) Localized positive charge and significant changes in bonding in positively-charged molecules reduces hole mobility. (5) The ETL material, as with other insoluble molecular materials, must be easily evaporable and should not crystallize. (6) ETLs should be unreactive in operating devices.

9.3.2 Molecular hole transporters

The choice of hole transporting molecule is not as clear cut as for the electron transporting layer. Examples of HTLs include diphenyl-biphenyl and related compounds such as N,N-bis(1-naphthyl)-N,N-diphenyl-1,1-biphenyl-4,4-diamine (NPD) shown in Figure 9.14. As with ETL’s, the primary objective in design of a hole transport material is to obtain a delocalized hole density across an entire positively-charged molecule while a localized electron would occur in a negatively-charged molecule. In addition, a lower binding energy of the HOMO and LUMO states relative to the vacuum level make hole injection easier in these materials.

A key issue in hole transporter molecule stability has been found to be the degree of crystallinity of the molecules and the grain size once crystallization occurs. Reduction

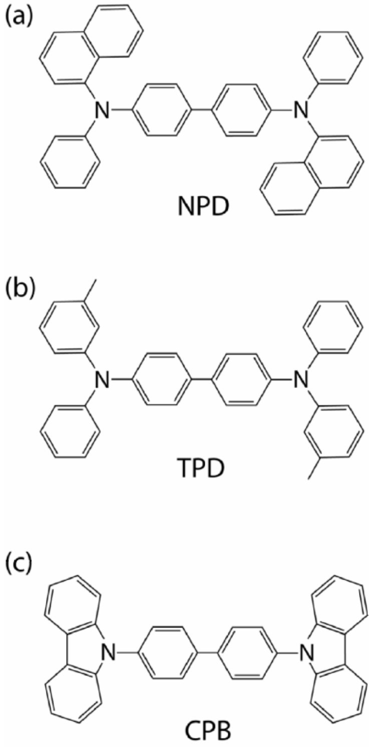

Figure 9.14: Shows the chemical structure of three hole transporter molecules, (a) *N,N’*-diphenyl-*N,N’*-bis(3-methylphenyl)-1,1-biphenyl-4,4’-diamine or NPD, (b) *N,N’*-di(naphthalene-1-yl)-*N,N’*-diphenyl-benzidine or TPD, and (c) 4,4’-N,N’-dicarbazole biphenyl or CPB.

in tendency to crystallize can be accomplished by reducing molecular symmetry (necessary for close molecular packing), increasing the molecular weight, and increasing the glass transition temperature. All of these differences occur in NPD compared to a similar molecule TPD (Figure 9.14b). TPD has a methyl-phenyl group in place of the napthyl groups of NPD. The glass transition temperature of TPD is 63°C as compared to 95° for NPD. NPD is also more rigid. Both effects reduce the self-diffusion coefficient and tendency to crystallize for NPD.

In addition to crystallization effects, degradation of the devices is increased with an increased barrier to hole injection from the anode. This is a persistent problem in OLED's. There are no metals with high enough work functions to make ohmic contacts to the HOMO states in typical organic compounds. Transparent conducting oxides (TCOs) are the best hope and most commonly used. N-type TCOs result in high barriers to hole injection but are common and easy to produce. P-type TCOs are rare, far less conductive, and little explored to date. The high barrier with n-type TCOs requires a large electric field to induce sufficient carrier injection. This, in turn, requires a large bias voltage to turn on the device. The large bias is inconvenient but more significantly the kinetic energy of injected carriers increases with increased bias and raises the probability of a carrier causing damage to the molecular structure of the HTL.

Charge-injection damage is a major source of degradation of OLEDs. Clear evidence of the effect of injection barrier on device lifetime was obtained by Adachi et al. [12] as shown in Figure 9.15. In this study the degradation of a large number of possible hole transport layers having a variety of HOMO energies were studied. A roughly linear decrease in lifetime with an increase in HOMO binding energy was found, demonstrating the importance of the HOMO state energy in charge injection degradation. This also illustrates the problem with producing blue-emitting OLEDs. To produce a blue-emitting device, the HOMO/LUMO gap must be at least in the blue spectral energy range. Achieving a high HOMO/LUMO gap generally requires a deep HOMO state. It will be necessarily more difficult to inject holes into such a state and the consequent lifetime of the device will be shorter.

Fortunately, charge injection degradation can be reduced at least in some devices. One common method is to introduce a cascade of materials with increasing HOMO binding energies, breaking the total energy barrier for injection of holes into a series of smaller steps. Many different materials are used in these cascades. Some examples appear elsewhere in this chapter.

Particularly attractive materials for assisting charge injection are the metal phthalocyanines. It has been shown that the introduction of one or two metal phthalocyanine layers between the ITO transparent anode and the hole transport layer can dramatically increase the device lifetime at a given luminosity. The most commonly-used of these molecules is copper phthalocyanine (CuPc), shown in Figure 9.16. In addition to mediating hole injection, it is thought that diffusion of

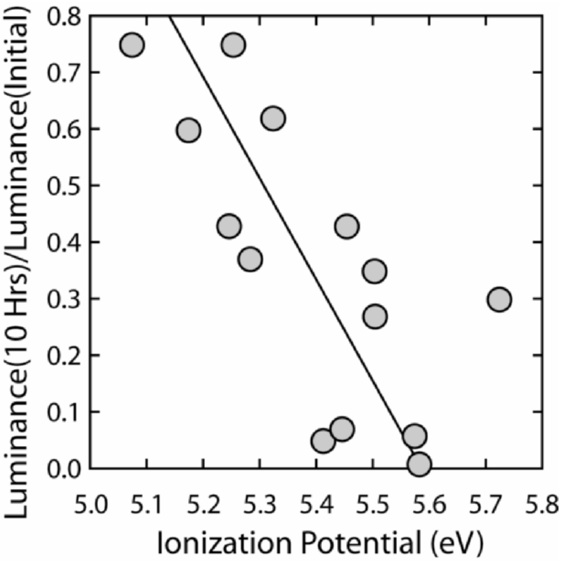

Figure 9.15: Shows the lifetime of OLED devices based on various compounds with a variety of ionization potentials. The lifetime here was determined as the output of the device after 10 hours relative to the initial luminance. Reused with permission from Chihaya Adachi, Kazukiyo Nagai, and Nozomu Tamoto, Applied Physics Letters, 66, 2679 (1995). Copyright 1995, American Institute of Physics.

atoms from the ITO into the HTL can degrade performance. The CuPc molecules appear to be relatively insensitive to this type of damage.

Additional evidence for the effect of metal-Pc molecules on the barrier to charge injection at the anode has been obtained by Zhu et al.. [13] They observed in ITO/MPc/TPD/Alq_3/Mg-Ag devices that the operating voltage decreased in the sequence H_2Pc > SnPc > VOPc > NiPc > PbPc > CoPc > FePc > CuPc > ZnPc. This trend is consistent with a corresponding change in the energies of the HOMO states of these compounds. Thus, substitution of the metal ion in the compound provides a direct control of the injection barrier. Of the various phthalocyanines listed above, CuPc has been found to have the best overall combination of low charge injection barrier and resistance to chemical reactions and other degradation mechanisms. Note that the device requires the TPD or other HTL to block electron injection from the Alq_3 into the MPc. Attempting to produce a device without the HTL results in a high current but a low luminescence due to a failure of moving charges to meet and recombine radiatively. [14]

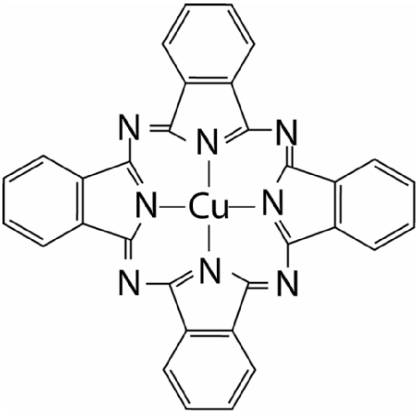

Figure 9.16: Shows the chemical structure of the copper phthalocyanine molecule. Other MPc molecules referred to in the text are similar with different metal ions in the core of the molecule.

9.3.3 Dye molecules

The overall performance of OLEDs can be dramatically improved by the use of dye molecules. These small molecules efficiently trap electrons and holes (ie: carbanions and carbocations) and have high radiative recombination rates relative to non-radiative decay processes. One can quickly see why this would be effective in a device as the dye molecule can be optimized for recombination, while the HTL and ETL layers can be optimized for carrier transport, carrier injection and chemical stability without having to worry about radiative recombination. From the discussion in Section 9.2, it is known that many molecules exhibit low radiative recombination rates due to the symmetries of their HOMO and LUMO orbitals, resulting in disallowed optical recombination pathways. The "solution" to the problem is to dissolve dye molecules optimized for emission in one or more of the transport layers.

In a full color display, it is necessary to have efficient light emission from individual devices with different colors (red, blue, and green). Dye molecules allow the color of the light emission to be tailored by changing the dye without affecting the composition of the remainder of the device. This means that the HTL and ETL layers and any buffer layers surrounding the contacts can be optimized for high device performance without worrying about the resulting wavelength of emitted light. The only requirement is that the HTL and ETL have a higher HOMO/LUMO energy gap than the highest energy photons to be emitted (blue). This requirement is not trivial, as the stability of molecules generally decreases as the HOMO/LUMO gap increases. Common matrix materials for the HTL and ETL are TPD and Alq_3, which have HOMO/LUMO gaps of 3.1 eV for TPD and 3.3 eV for Alq_3 in the green portion of the spectrum. The problem may be finessed somewhat by adding higher-gap barrier layers such as BCP between the Alq_3 and the emissive layer. The ability to change the light emission wavelength without changing the remaining materials in the devices certainly simplifies manufacturing. Dye molecules generally emit in a narrower range of wavelengths than do the HTL and ETL layers. Narrower emission lines mean purer colors. More saturated (very red, blue or green) light emission results in more vivid color displays. Finally, because dye molecules increase light emission efficiency, less drive current is required. This increases device lifetimes.

Based on the above, criteria important in the selection or design of a dye molecule include:

1. The dye should trap free carbocation and carbanion defects from the surrounding matrix and efficiently convert these to excitons.
2. These excitons should remain on a single dye molecule, rather than being distributed over multiple molecules. (The carbocation and carbanion should both be on the same molecule.)
3. The excitons should decay radiatively. To accomplish this the exciton lifetime should be relatively short.
4. Dye molecules should be designed to make use of energy in triplet states as well as singlet states for luminescence.
5. There should be a high solubility of dye molecules in the matrix.
6. The dye color should be strongly saturated and the emission line should be sharp.
7. The dye molecule should be chemically stable in the excited state (i.e. when an exciton is present).

In a typical high-efficiency OLED, see Figure 9.17, the majority of the formation of excitons and light emission occurs in the ETL or in a special recombination layer material between the ETL and the HTL (CPB in the example shown in Figure 9.17). Generically, the HTL is less favored because the exciton energy is lower (excitons are more stable) in ETLs compared to HTLs. If we ignore the possibility of a recombination layer and focus on a simple HTL/ETL heterojunction device, the general exciton formation process is as follows. Holes are injected from the HTL into the ETL. These holes are not highly mobile and soon encounter either a dye molecule or an electron. In the former, the hole is trapped on the dye molecule and awaits the arrival of an electron. In the latter case, an exciton is formed immediately. This exciton can decay radiatively. However, the host is not optimized for such a process. Therefore the exciton lifetime is relatively long. For sufficient dye concentrations the exciton will diffuse to and become trapped on a dye molecule before it decomposes or decays in the host ETL.

The details of the mechanisms of carrier and exciton trapping by the dye are beyond the scope of this text but may be found in the references. It is sufficient here to state that the efficiency of trapping by the dye molecule depends upon its shape and charge distribution; the shape, charge distribution and organization of the host; and the host/dye bonding interactions. These control the distribution of dye molecules, their orientation relative to the matrix molecules, and the interaction of the electronic states among the molecules. The effectiveness of a dye at trapping carriers can be related to a quantity known as the Förster radius (~3 nm for most dyes). [16] Therefore, dye design criterion (1), above, can be represented in part as a requirement for the dye to have a large Förster radius.

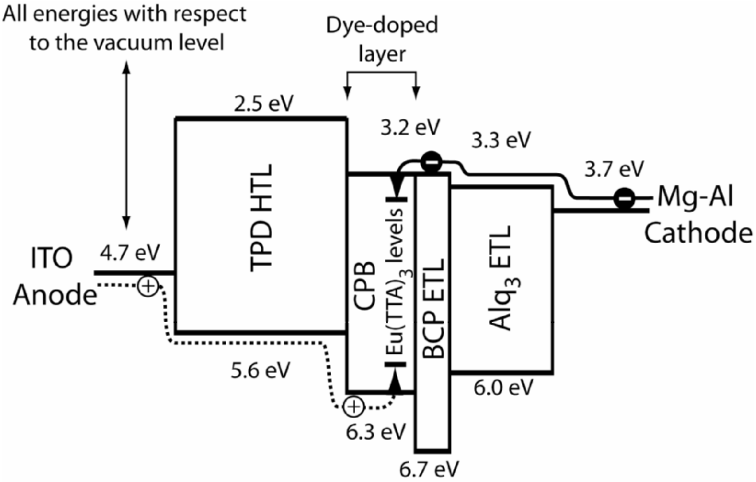

Figure 9.17: A band-edge picture of an efficient tested OLED device biased for flat bands. This device contains both TPD and Alq_3 hole and electron transport layers, a CPB hole transport layer (see Figure 9.14) hosting $Eu(TTA)_3$ dye molecules, and a 2,9-dimethyl-4,7-diphenyl-1,10-Phenanthroline (BCP) buffer layer. The buffer layer serves to prevent injected holes from entering the Alq_3. The TPD/CPB junction acts as an electron barrier. Redrawn with permission from Chihaya Adachi, Marc A. Baldo, and Stephen R. Forrest, Journal of Applied Physics, 87, 8049 (2000). Copyright 2000, American Institute of Physics.

Dye molecules have been shown to greatly increase the photon output of OLEDs, as shown in Figure 9.18. However, there is a strong peak in the luminescence as a function of dye concentration. At very low concentrations a minority carrier may not encounter a dye molecule before it recombines, so the contribution of the dye to luminescence is small. Initially, increasing the dye content increases the rate at which charges are trapped and the rate at which excitons are formed. The peak in luminescence will occur where virtually every minority carrier is trapped on a dye molecule before it can decay in the matrix. The average spacing between the dye molecules at the peak efficiency is near the Förster radius.

At higher concentrations the luminosity decreases gradually for several reasons. A pure dye molecule matrix is not an effective light emitter. At high dye concentrations, carbocation/carbanion excitons become delocalized over two dye molecules. This state is not strongly bound (indeed, it is not a ground state of the system) and the carbocation and carbanion can separate relatively easily. The delocalized exciton also tends to decay more frequently by non-radiative processes, reducing luminescence. Thus, it is evident that there is a positive influence of the presence of the non-dye matrix. Dye molecules are often not very soluble in the organic matrix and phase separation can occur as the concentration increases. Because dye molecules are not effective emitters in groups, the resulting aggregates of dye species show decreased luminosity. At high dye concentrations, the radiation spectrum also broadens, producing a less pure color and giving a more pastel hue to the device.

Based on the above discussion, we can see that the ideal situation is to have individual dye molecules separated from each other by the host matrix but at a sufficiently high concentration that no recombination occurs in the host. The matrix supplies carbocations and carbanions to the dye, which traps and efficiently recombines them radiatively. The most effective method for trapping charges and forming excitons is for the dye molecule to have a lower HOMO/LUMO gap energy and to have the HOMO lie above and the LUMO below the corresponding states of the host material. This situation is shown schematically in Figure 9.17. However, this also implies a larger HOMO/LUMO gap in the matrix for a given emission energy, which reduces device stability and increases contract problems.

Because the host matrices are typically either electron or hole transmitters and relatively poor at transmitting the other type of charged defect, most of the recombination occurs near the heterojunction, and usually on the ETL side. Therefore, the most critical location for dye molecules is generally in the ETL near the heterojunction. The situation can be optimized by providing a thin recombination layer between the ETL and the HTL in which the dye is located. This layer can be designed for high dye solubility and effective transfer of charges to the dye molecules, rather than for stability with respect to contacts or effective hole or electron transport properties. Such a layer is shown in the device in Figure 9.17.

Additional advantages of using dye molecules are that they decrease the tendency of the host matrix to both crystallize and agglomerate. In agglomeration, a layer forms in clumps or hillocks rather than remaining uniform and flat. Such clumping concentrates current in the thin regions where the resulting fields are higher. This causes rapid degradation of the device.

A large number of molecules have been developed for use as dyes in OLEDs. For a detailed discussion see Shoustikov et al. [16] or the less detailed Chihaya et al. [18] or Kanno et al.. [19] Examples of the more popular molecules or those that provide relatively saturated colors (as of this writing) are shown in Figure 9.19. The most common way to represent the color of a dye molecule is on a chromaticity diagram.

The location of the dye molecules with structures given in Figure 9.19 on such a diagram is shown in Figure 9.20. Molecules luminescing near the corners of the triangular curve in the diagram provide the most strongly saturated red, blue, and green colors. Points closer to the center of the diagram provide more pastel colors.

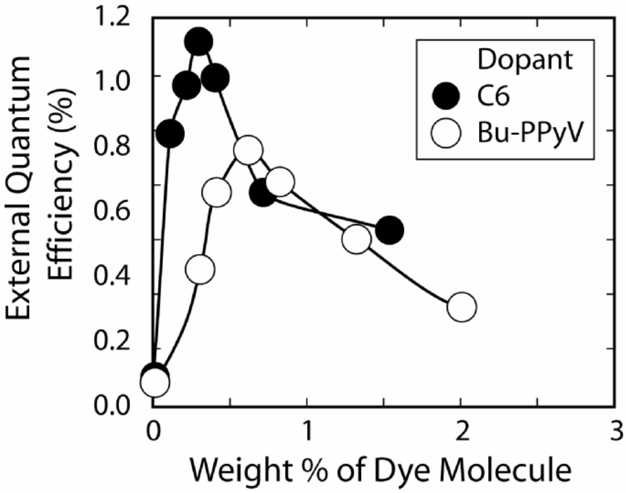

Figure 9.18: Efficiency of OLED's formed with coumarin 6 (C6) [see Figure 9.19] and poly(3-n-butyl-p-pyridyl vinylene) (Bu-PPyV) dyes in a polyvinyl carbazole (PVK) hole transport layer. The remainder of the device included an electron transport layer and ITO and Mg-Al electrodes. With permission after Shoustikov, Andrei A.; You, Yuijian; Thompson, Mark E.; "Electroluminescence color tuning by dye doping in organic light-emitting diodes." *IEEE J. Sel. Topics in Quantum Electronics* 1998; 4: 3-13. Copyright [1998] IEEE

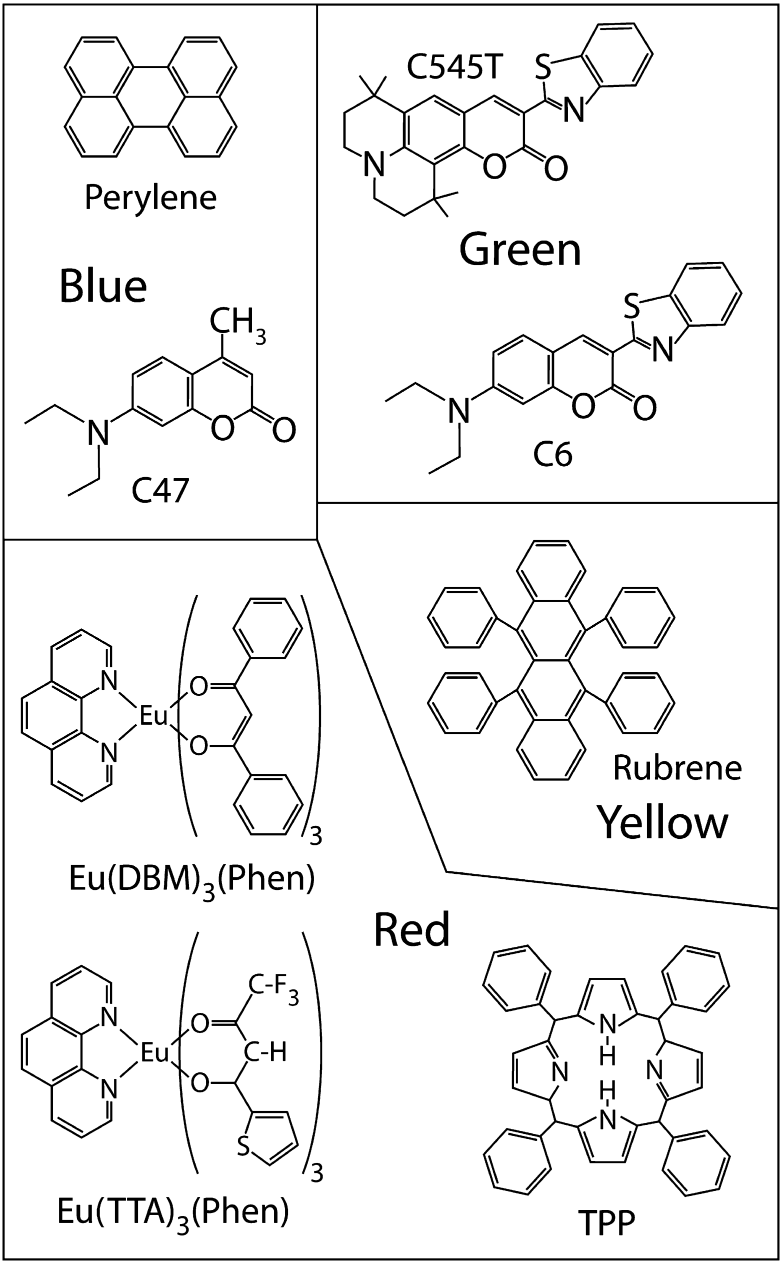

Figure 9.19: The chemical structures for selected compounds used as molecular dyes.

For a full color display, luminescence near the corners of the diagram is optimal. For an organic "light bulb", emission near the center of the diagram (white emission) would be acceptable or even preferred.

In recent work, a significant improvement (roughly a factor of three) in luminescence efficiency was obtained by adding rare earth transition metal complexes to the device. These exhibit efficient phosphorescence (a slower form of fluorescence which does not require spin conservation). The high electron density in the rare earth mediates electron spin transitions and mixes the singlet and triplet states, allowing conversion of triplet to singlet states. What makes the situation more efficient is co-doping of a host matrix with both a phosphorescent and a fluorescent material. (The fluorescent material is a standard dye molecule such as those shown in Figure 9.19.) The phosphorescent material captures excitons from the host, and passes the singlet state of the exciton to the fluorescent material. Thus the concentration of singlet states in the fluorescent material is enhanced significantly, along with the luminescence intensity of the device. Several examples of such systems have been described recently. For example, M.A. Baldo et al. discuss the use of Ir(ppy)$_3$ (see Figure 9.21) as a phosphorescent spin mediator leading to luminescence of a separate dye

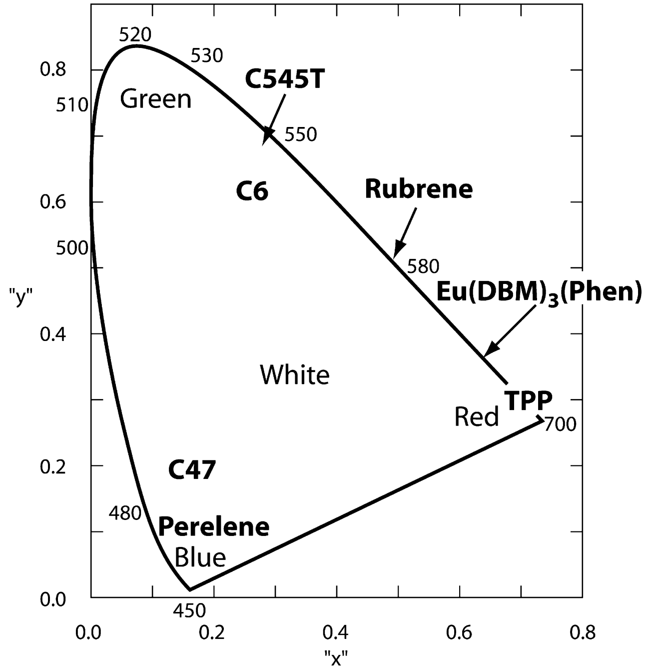

Figure 9.20: A chromaticity diagram for some of the more common dye molecules shown in Figure 9.19. Note the lack of a really saturated green dye.

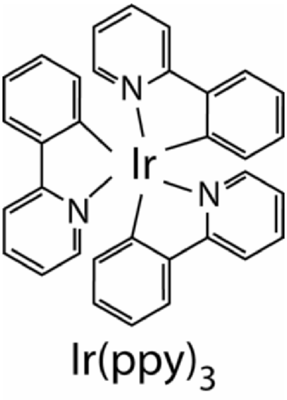

Figure 9.21: The chemical structure of Ir(ppy)$_3$ used as a phosphorescent mediator converting triplet state excitons to singlet states.

molecule. [20] These rare-earth complexes are now used ubiquitously both as dyes themselves and as triplet-singlet mediators for other materials. As dyes they tend to produce wide emission spectra and are used primarily with other compounds to produce white-emitting devices.

9.3.4 Molecules for thin film transistors

Organic thin film transistors have achieved performances in excess of those of the amorphous Si devices described in Chapter 8. The highest performance devices have been based on molecular rather than polymer species. The best overall results have been obtained with pentacene (see Figure 9.22a), as described in Section 9.2.2. However, α-sexithienyl (see Figure 9.22b) has also been used successfully. Both of these molecules have a tendency to form relatively large crystalline regions with grain sizes up to one micron estimated from atomic force microscopy analysis. Crystallinity is essential to high carrier mobilities. Unfortunately, there is a cost in weak bonding of the film to the substrate when the film is deposited under conditions yielding good crystallinity. To improve adhesion in the presence of high crystallinity, Jackson and coworkers have shown that a self-assembled monolayer of octadecyltrichlorosilane between the pentacene and the SiO_2 underlayer improves the performance of the devices. [5] The field-effect mobilities obtained in pentacene devices of 2 $cm^2\ V^{-1}s^{-1}$ is in the range anticipated for the upper limit to mobilities for such materials. [21] This indicates that the well-ordered polycrystalline pentacene layers obtained are not primarily limited by their microstructure. Indeed, while most organic materials exhibit thermally activated hopping conduction, the highest mobility values in pentacene suggest a transition to temperature-independent band-like conduction. Perhaps this is not surprising if the molecules are crystallized and lie very close to one another such that their molecular orbitals can overlap to form bands.

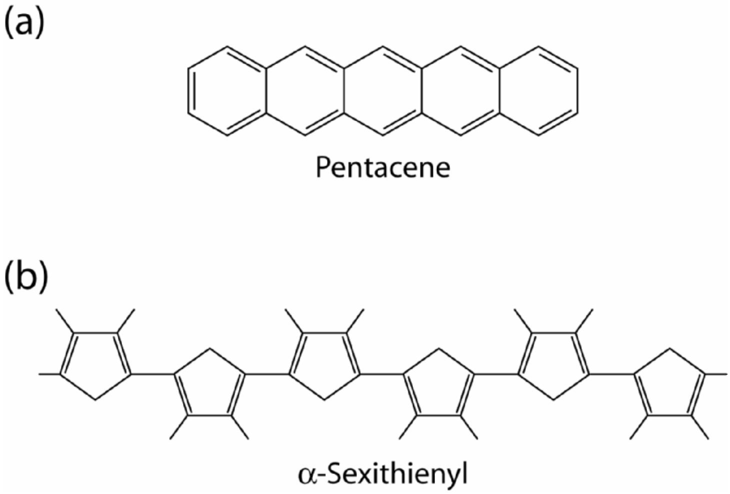

Figure 9.22: Shows the chemical structures of the two most popular molecules for organic thin film transistors, as discussed in the text.

One of the significant problems facing molecular organic TFTs is the formation of coulomb blockades at Au source and drain contacts. These have been described by Schoonveld et al. [22] and can have a significant effect on the apparent mobility of carriers in the device. The solution to this problem almost certainly involves more careful selection of the contact metallization materials.

9.4 POLYMER OPTOELECTRONIC ORGANICS

In spite of the generally higher performances achieved in light-emitting and thin film transistor devices with molecular organic materials, organic polymers have generally been the choice for demonstration of larger scale devices and product manufacturing. Polymers have superior processing options primarily because they are relatively soluble in organic liquids (at least as compared to the molecular species described above). This makes spin-coating, stamp printing, and ink-jet printing possible. The latter two, in particular, allow fabrication of devices without relying on lithography – a significant benefit. Most of the issues related to polymer electronic materials design are similar to those for molecular species. However, polymer design also includes significant work on solubility. Some of the more popular molecules for light emitting and thin film transistors are discussed below, along with general aspects of their design.

The most significant optoelectronic requirements for improving polymer devices currently include reducing the turn on voltage, lowering operating current by improving efficiency, and balancing electron and hole injection into the device. In Section 9.3, we saw that the introduction of barriers to specific carriers through control of the electron affinity of the molecules can effectively prevent carriers of either type from crossing the entire device. Furthermore, we saw that similar control of orbital energies can reduce carrier injection barriers. This lowers the voltage necessary for a given level of current injection and hence the input power. Likewise, increasing carrier mobility reduces this voltage by lowering the resistance of the device. Finally, more efficient luminescent recombination mechanisms are required to reduce injection currents at given luminosities. Increased luminosity is achieved by tailoring the polymers by the addition of specifically designed efficient fluorescent materials or functional groups. As with molecular species one may also dope the matrix with molecular species such as $Ir(ppy)_3$ or related polymeric materials to harvest energy in triplet states as discussed in Section 9.3.3. For switching devices, carrier mobility and material stability are important as for molecular species.

The above requirements can be summarized in the following general design goals for polymeric optoelectronic materials:

1. Control of HOMO and LUMO energies relative to the vacuum level.
2. Control of crystallinity and molecular organization for improved carrier transport characteristics.
3. Achieving a large range of ratios of carbocation and carbanion mobilities to provide effective electron and hole transporting materials capable of resisting transport of the other species.
4. Control the luminescent wavelength and maximized radiative relative to non-radiative recombination of excitons.
5. Maximization of solubility of the polymer and enhancement of other aspects of processability.

Molecules exhibiting particularly desirable properties in these respects are discussed below. Issues directly related to carrier injection and stability at contacts are deferred to Section 9.5. As we shall see, all of these properties may be controlled by addition of functional groups to the sides of the fully conjugated polymer chains.

9.4.1 Polymers for organic light emitting devices

In polymers, less distinction is drawn between primarily electron-transporting materials and primarily hole-transporting materials. Indeed, some molecules can be functionalized to accept carbanions efficiently in one region and carbocations in another. Because the molecules are continuous strands the two ions can move along the chain backbone without necessarily requiring interchain transfer. Self-assembled functional blocks in the molecule can also reduce the need for multiple molecules. In spite of this, at least two polymer layers are generally used in devices to optimize electron injection from the cathode and hole injection from the anode. Because of the smaller level of distinction between the materials, this section discusses both electron and hole transmitting polymers together.

The quintessential polymer optoelectronic material is poly-paraphenylene vinylene, PPV, with the structure shown in Figure 9.4. It is primarily used as an electron-transporting material but can be used in single-layer devices as well. A better description might be to say that PPV is used primarily on the cathode side of two-layer devices and acts as the primary recombination layer. Pure PPV is a rigid rod polymer with a strong tendency to crystallize and very low solubility. Therefore, it must be deposited in another form and polymerized on its intended substrate. This is extremely inconvenient from a processing standpoint. Therefore, there has been a strong driving force to engineer PPV to improve its properties. The currently most popular electron transporting (or cathode side) molecular organic semiconductors are derivatives of PPV based on functionalizing the vinyl or phenyl groups to meet the design criteria outlined above.

One of the most successful of the altered molecules is poly(2-methoxy-5-(2’-ethylhexyloxy-)*p*-phenylenevinylene), or MEH-PPV. The basic structural unit of this molecule is shown in Figure 9.23. MEH-PPV has acceptable solubility in common solvents such as tetrahydrofuran (THF). MEH-PPV emits in the red-orange spectral range (which can be further modified as described below). While such colors are potentially useful in producing a full-color display, MEH-PPV is not satisfactory as a host for other fluorescent molecules. The 2.3 eV HOMO/LUMO gap [23] of PPV likewise prevents it from fluorescing above the green portion of the spectrum. Typically, further functionalization of MEH-PPV lowers the HOMO/LUMO gap, red-shifting the resulting emission and further restricting the range of applicability. This has contributed additional impetus to explore other non-PPV-based materials.

In recent years, materials based on polyfluorenes (PFOs), see Figure 9.23, have become increasingly popular as blue light emitters for the cathode side of OLEDs as they provide strong emissions in the 380-420 nm wavelength range. [Note that polyfluorene contains no fluorine atoms. It is based on the *fluorene* monomer, a carbon ring structure (Figure 9.23a).] The fluorene monomer can also be copolymerized with other monomers to alter its properties (in particular the fluorescent wavelength). As with the PPV materials, side chains can be added to modify the solubility and optoelectronic properties. In Figure 9.23a, two functional side groups on the PFO are designated by “R”. These can be as small as hydrogen atoms or as large as massive side chains. The most common side chains are short alkanes. The

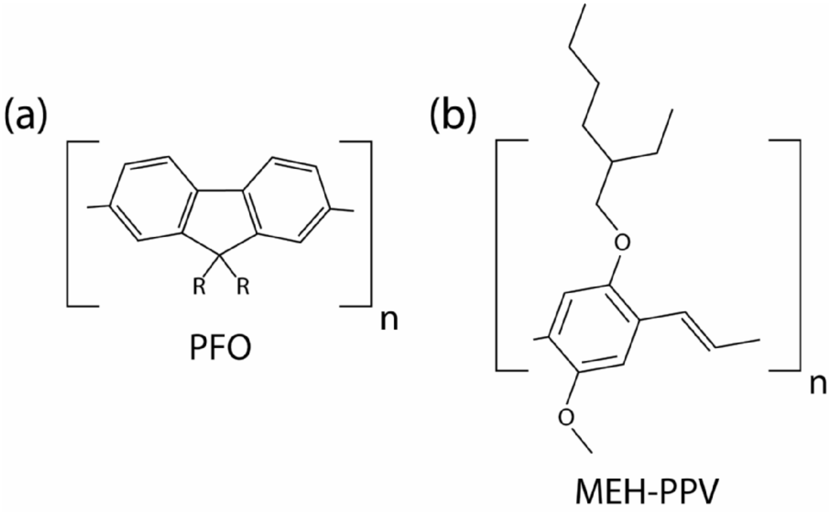

Figure 9.23: Chemical formulas for two molecules frequently used as electron-transporting and recombination layers in polymer light-emitting devices.

power of synthetic organic chemistry has been demonstrated effectively in the design and modification of light-emitting molecules such as PPV and PFO. As examples, let us briefly consider selected modifications of PPV in more detail.

The functionalization of PPV has been shown to allow control of electron affinity, HOMO/LUMO gap, and solubility. For example, the addition of alkoxy side groups, converting PPV to MEH-PPV increases solubility significantly. A difference in peak fluorescence wavelength is also obtained depending upon whether the side chain is an alkane or an alkoxy group (ie: whether the unit binding the side chain to the aromatic ring is a CH_2 or an O atom). The electron donating alkoxy groups result in a greater red shift in the resulting light emission. Likewise, electron donating or electron withdrawing groups can be added to the vinyl linkages to further modify the emission wavelength of the conjugated polymer backbone. For example, addition of electron withdrawing cyano (-CN) groups reduces the HOMO/LUMO gap and increases the electron affinity. This has been found to improve the luminescence of resulting devices significantly through changes in the efficiency of charge injection. (See, for example, N.C. Greenham, et al.. [24]) The cyano addition has a different effect depending upon whether the group is added closer to or farther from the alkoxy chains. The primary effect is through controlling twisting distortions in the π-bonding backbone of the molecule. The details of such polymer engineering are beyond the scope of this book. A discussion and detailed references concerning the engineering of side chain chromophores on PPV and their affect on the luminescent properties of the material may be found in van Hutten et al.. [25]

Fortunately, the design of such molecules can be aided significantly by quantum chemical calculations on model molecular segments (see, for example, Bredas et al. [1]). These methods permit effective prediction of the effect of specific side-group additions at specific locations on the optoelectronic properties of isolated molecules in both ground and excited states. The ability to predict the behavior of excited states is important as luminescence results from relaxation of these. The energy of excited states is closely coupled to changes in molecular conformation or organization upon excitation as noted in Section 9.1. For example, results suggest that PPV derivatives can become more flexible upon excitation, which can strongly influence the fluorescent efficiency and wavelength. Likewise, the stacking of molecules strongly influences the overlap of electron orbitals and contributes to intermolecular state luminescence. [25] This is in some senses unfortunate, as in amorphous molecular films a wide variety of chain packing arrangements occur and leads to broadened emission spectra and less saturated colors. Furthermore, it is difficult to assess the collective behavior of an amorphous polymer network from theory. The morphology and nanostructure of the resulting material becomes important in this case. Indeed, it is the interplay of nanostructure and properties that, in the end, makes a detailed prediction of the properties of the materials most difficult.

In addition to chemical methods used to design homogeneous polymers, all of the options of copolymerization and surface treatment have been applied to design of organic layers for optoelectronics. Subunits in the polymer chain can be optimized to accept electrons or holes or for recombination of excitons. Surface treatments can be used to orient the molecules on the substrate in the correct direction for optimal performance. These treatments can also be used to control the crystallinity or molecular nanostructure of the organic layer to some extent (or to a large extent in some cases), as was the case for pentacene self-assembled monolayers described above. Such modifications can be applied in both electron and hole transporting materials, which again blurs the boundary between the materials. Methods for engineering polymer subunits and copolymerization can be found in M.A. Fox. [26]

The results of copolymer engineering can be observed in the control of emission wavelength in PFO-related materials. PFO alone emits in the blue spectral region. To provide longer wavelength materials, PFO has been copolymerized with PPV-like (for red) or benzothiadiazole (BT) (green) units. An example of the resulting polymers, the performance of the devices, and full references may be found in I.D. Rees et al.. [27] Changes to the work function also occur with copolymerization. For example, PFO has HOMO and LUMO levels ~5.8 and 2.6 eV from the vacuum level, respectively, while the BT-PFO copolymer has corresponding values of 5.9 and 3.1 eV, lowering the injection barrier for electrons into the material. [27]

Although one can produce polymer OLEDs without an HTL, the performance of the device improves dramatically if a material specialized for hole injection from the anode is used. The HTL reduces the device operating voltage, increases lifetime, and

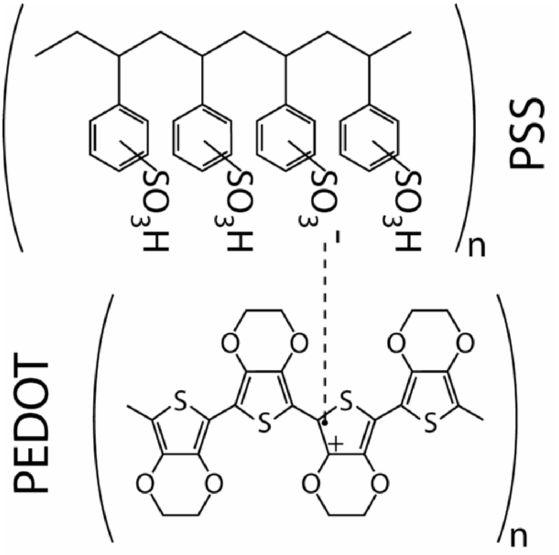

Figure 9.24: The chemical formula for the two components poly(3,4-ethylene dioxythiophene) (PEDOT) and poly(styrene sulphonic acid) (PSS) making up the PEDOT:PSS polymer blend used in contact with the anode and for hole transport in polymer OLEDS. Note that the two molecules bind together strongly as a double bond is broken in the PEDOT units and an electron is transferred to the PSS, resulting in release of a hydrogen atom (which may bond with the reactive radical site of the double bond. The molecules are held together, in part by the attraction of the ionic charges.

results in a better balance of hole and electron currents. The most popular anode-side material currently is poly 3,4-ethylene dioxythiophene (PEDOT), normally used in a polymer blend with poly (styrene sulphonic acid) (PEDOT:PSS). The structures of these molecules are shown in Figure 9.24. Note that PEDOT and PEDOT:PSS are relatively insoluble in their conventional forms and must be synthesized after precursors are deposited. Poly(aniline) or poly(thiophene) have also been popular for anode-contacting layers. These materials are highly conductive and optimized for efficient hole injection.

Comparisons of polymer OLEDs generally show an order of magnitude improvement in light emission efficiency for PPV-based devices when the surface of the ITO anode is treated with oxygen plasmas or acid cleaning methods (which modify the effective work function of the ITO surface). However, a thousand fold improvement results from the use of hole injection layers such as PEDOT:PSS.

Some PFO-like materials can also act as acceptable hole-injection layers as well as recombination layers fluorescing in the blue. An example of such a material is poly(9,9-dioctylfluorene-*co*-bis-*N*,*N*8-(4-methoxyphenyl)-bis-*N*,*N*8-phenyl-1,4-phenylenediamine) [PFMO], shown in Figure 9.25. [28] These modified PFO's have lower HOMO and LUMO energies relative to the vacuum level and therefore have lower hole-injection barriers.

Many other materials have been considered in polymer OLEDs. The results are reflected in the dramatic gains in performance of the devices as shown in Figure 9.10. All of these materials combine multiple functions (as compared to molecular materials where each separate constituent molecule has a specific purpose). The molecules are designed by quantum chemical methods supplemented with a considerable experience base among synthetic chemists. The final materials represent a compromise between performance and manufacturability. The most successful materials in manufactured devices are based on soluble polymers.

9.4.2 Polymers for transistors

The polymers used for organic thin film transistors are chemically similar in general to α-sexithienyl and include materials such as poly(3-hexylthiophene) (P3HT) and related compounds (see Figure 9.26). This material has functional groups incorporated onto the thiophene units as shown in the figure. However, there are two possible arrangements of these units, known as "head-to-head" and "head-to-tail", see Figure 9.26. Polymers consisting of the head-to-head arrangement can stack much more regularly and produce higher carrier mobilities in solution cast layers. Therefore, the head-to-head moieties are preferred for polymer TFTs. For a discussion of devices based on these materials, see Z. Bao et al.. [29]

As in the case of OLEDs, the primary driver for considering polymeric materials for OTFTs is the possibility of rendering them soluble by addition of appropriate side chain functional groups. The orientation of the molecules in the resulting films

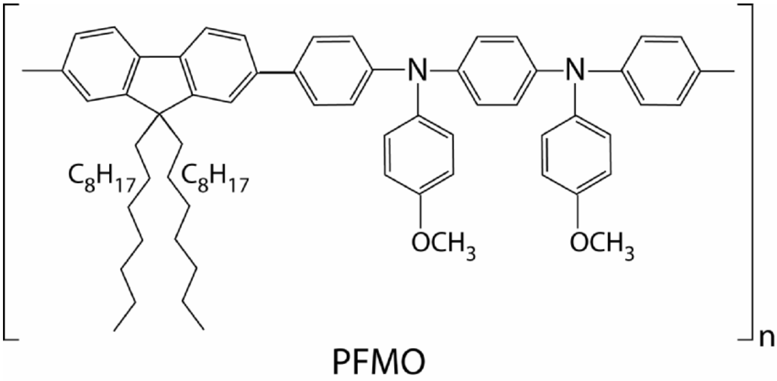

Figure 9.25: The chemical structure of poly(9,9-dioctylfluorene-*co*-bis-*N*,*N*8-(4-methoxyphenyl)-bis-*N*,*N*8-phenyl-1,4-phenylenediamine) (PFMO), a hole-transmitting material which fluoresces in the blue region of the visible spectrum.

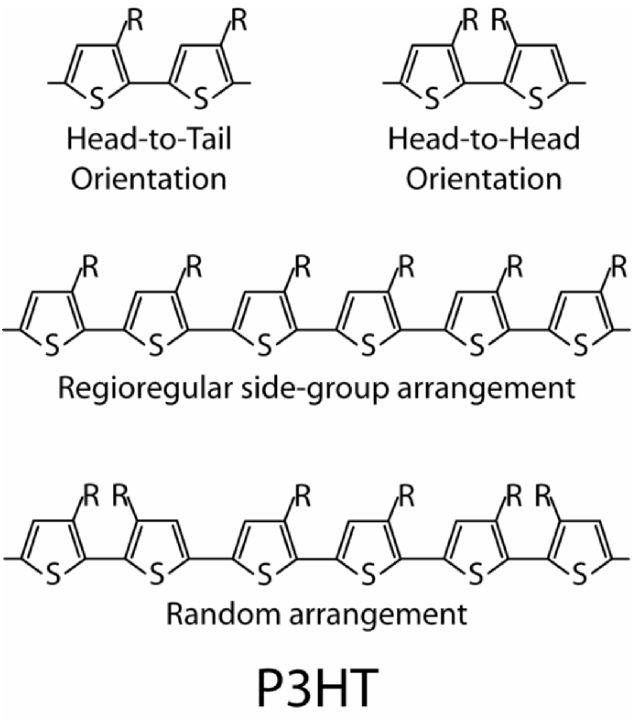

Figure 9.26: The chemical structures of poly(3-hexylthiophene) (P3HT) showing the head-to-head, and head-to-tail arrangements of functional groups. The head-to-head arrangement can be present in large blocks in a molecule (regioregular) or the two arrangements can be mixed randomly.

depends upon the solvent from which the material is cast. For P3HT, the best organization has generally been obtained using chloroform. The organization of P3HT layers on surfaces can also be influenced by surface treatments. When the layers are deposited on SiO_2 surfaces, stronger interactions and better organization can be obtained when the hydroxyl termination of typical SiO_2 is replaced with an organic surface termination. Such a surface generally improves carrier mobilities in P3HT on SiO_2.[30]

The architecture of devices based on polymer organic materials are similar to those described for molecular organic devices (see Figure 9.11), although devices using polymer dielectrics have also been produced. The thiophene compounds and most materials used for OTFTs are p-type (majority hole conductors) and the devices generally operate in enhancement mode. In other words, the conductivity is increased by the applied bias in the device. The performances of the polymer semiconductors in these devices are generally lower than for their molecular cousins by nearly two orders of magnitude. The highest field-effect mobilities are typically 0.1 $cm^2 V^{-1}s^{-1}$ with device on/off current ratios of 10^6. [30] The difference in performance of the polymers relative to the molecular species is significant in that the polymers currently under-perform the competing a-Si devices now employed in flat panel displays, while molecular device results are comparable or even superior to a-Si devices. The primary reason for the underperformance of the polymers is the lack of well-organized crystals. Consequently, carrier mobilities remain very low and limited by interchain hopping rather than intrachain transport. As for amorphous silicon based thin film transistors, polymer-TFT's can exhibit instabilities. Unlike the a-Si TFT's, these instabilities result from interaction of contaminant gases with the molecules. Therefore, a high-quality hermetic seal is required under inert gas conditions to prevent contamination with problem gases.

9.5 CONTACT TO ORGANIC MATERIALS

As noted above, a major problem facing designers of organic electronic devices is the contacts to the organic semiconductor, especially when the HOMO-LUMO gap is large (which it generally is). Contact to wide-gap materials is a generic problem for all electronic devices – contacting wide-gap semiconductors is much more difficult than contacting narrow-gap materials. Consequently, special care needs to be devoted to the materials selection. In the case of organic materials, as compared to conventional inorganic semiconductors, a further complication is the relative instability and reactivity of organic materials as compared to inorganics. Some organic materials are more sensitive than others. For example, PPV degrades by oxidation following charge injection more rapidly than does Alq_3. The issues in cathode and anode design differ significantly and are therefore considered separately in the following sections.

9.5.1 The cathode contact

Charge injection from the cathode into the organic layer can be viewed as a process of thermionic emission combined with tunneling of electrons from the metal into the organic material, as shown schematically in Figure 9.27. However, the situation is complicated by the low mobility of carriers in the organic material. Electron injection at the cathode results in reduction of the organic molecule and formation of carbanions, as described in Section 9.1.1. One can rapidly reach a point of so heavily reducing the organic molecule locally that further charge injection is inhibited pending diffusion of the carbocations away from the cathode. At the same time, the accumulation of negative charge reduces the electric field driving charge injection and contributes to a back diffusion of charge into the cathode. Over-biasing the system to encourage charge injection and diffusion, however, provides increased opportunities for creating energetic charges, stimulating chemical reactions and reorganizations, and consequently to materials degradation.

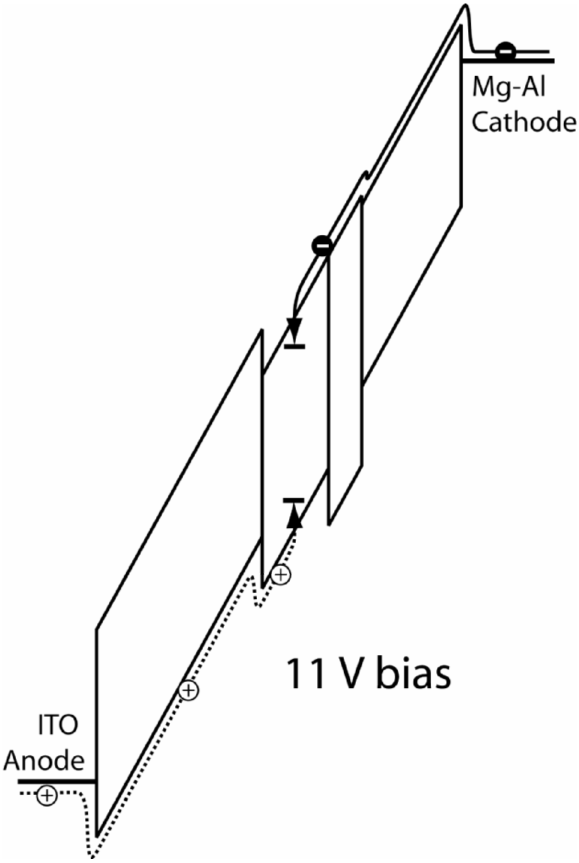

Figure 9.27: Shows the effect of bias on the band-edge diagram sketched in Figure 9.18, assuming that all organic compounds are equally conductive (and therefore the electric field in the organic layers is equally distributed).

Traditional cathodes use low work-function metals such as Ca. These have energies comparable to the LUMO energy into which electrons are injected. Any such low work function metal is naturally highly reactive, rendering the contact intrinsically unstable. Not surprisingly, reaction of the Ca electrode with the organic material degrades the device. It has been found that some preliminary oxidation of the electrode material is necessary prior to formation of the organic layer to avoid damaging reactions. Unfortunately, the cathode is not always the first layer formed and so pre-oxidation is not straightforward. When the cathode is the last layer produced, deposition of a reactive metal such as Ca often yields a non-functioning device. As a consequence, most devices are based on the more stable Mg or Mg-Al alloys. These provide an acceptable contact material with adequate stability.

An interesting alternative cathode, ZrC was explored by Sheats et al.. [31] ZrC has a low work function (between Ca and Al) and is unreactive. For example, it is highly stable in air for long times. Like many other transition-metal carbides, it has a good electrical conductivity. These factors make it appear a nearly ideal contact material. Indeed, good electrical results were obtained for ZrC cathode contacts to MEH-PPV. Unfortunately, the devices showed low luminescence efficiency, possibly because of defect formation near the contact in the organic layer. Likewise, the lifetimes of the ZrC based devices were relatively poor. Overall, this has led to the abandonment of ZrC as a contact material. Further research might find a solution to the observed problems.

The tendency to form an electrostatic dipole layer at the cathode junction that resists charge injection should be counteracted by use of a very low work function metal (with Fermi energy above the LUMO of the organic) that will supply electrons to the LUMO. This should spontaneously reduce the conjugated structure of the molecule and lead to a negative charge on the organic molecules near the contact. The large number of potentially reducible double bonds in the organic material restricts this dipole to the interface. Thus, no depletion region is found associated with the heterojunction.

In some cases, the reverse situation is found, in which electrons spontaneously transfer from the organic material to a higher work function metal. Again, there is no observable depletion layer and a positive charge occurs on the surface of the organic material. Both of the above cases result in interface dipoles. It is also possible to find no spontaneous charge transfer across the interface and no resulting dipole when the Fermi energy of the metal lies in the energy gap of the organic material. However, in practice, surface and interface states result in dipoles, even in these situations. [32]

It should be possible to create a favorable dipole at the contact capable of promoting charge injection by the application of an appropriate material in the interface. For example, an ionic (polar) compound could be inserted in an orientation in which the dipole of the ionic material would cancel out the interfacial dipole. This is one possible mechanism behind the success of LiF as an interfacial layer between Al and many organic compounds. Indeed, a thin layer of most alkali fluorides, oxides, or sulfides (in other words, strongly polar compounds) is found to lower the charge injection barrier, although LiF is the most popular. A discussion and detailed references may be found in N.K. Patel et al.. [4] A similar improvement has been observed by the use of elemental Li metal in contacts to Alq_3. This allowed a transparent cathode to be fabricated joining Alq_3 to ITO through layers of 2,9-dimethyl-4,7 diphenyl-1,10-phenanthroline and elemental Li. [33] However, the reactivity and diffusivity of the Li may make such contacts relatively less stable over the longer term and their ultimate performance remains to be determined.

9.5.2 The anode contact

In a typical light-emitting device, at least one of the contacts must be transparent to allow the emitted light to escape. In the case of OLEDs, this is usually the anode. In general, the anode has been fabricated from indium tin oxide, $(In_2O_3)_{1-x}(SnO_2)_x$, [ITO]. This material has a high electrical conductivity and a high transparency to visible light, although it absorbs substantially in the infrared due to the high concentration of carriers. ITO can also be viewed as a degenerately-doped n-type wide-gap semiconductor. It is commonly used as a transparent electrode in many devices including current flat-panel displays. The problem is then to couple this material to the organic layers into which holes are to be injected. ITO is used on the HTL side of the device because it has a relatively high work function. It is not usable as a cathode material, in spite of its heavy n-type doping, because of the barrier to electron injection into the LUMO state that would result for most organic compounds.

Anode contacts to hole transporting molecular layers were discussed briefly in Section 9.3.2. To reiterate, it is often found that metal phthalocyanine compounds effectively mediate the injection of holes from ITO into hole transport layers. (One could also say oxidation of carbocations in the HTL with net transfer of an electron from the HTL into the ITO.) Some experiments have suggested that multiple layers of phthalocyanines based on different metals, and hence having different HOMO state energies, can further reduce the injection barrier. The basic method in use in these cases is to provide a staircase of small barriers up which a hole can climb more easily than would be the case for a single large step. The low mobility of holes in the organic interlayers comes in handy here as it reduces the rate at which holes return to the contact.

For polymer-based devices, conducting polymers such as polyanaline and polythiophene have been used extensively as anodes. These are naturally p-type (hole conducting) materials produced by oxidation of conjugated molecules and thus are naturally suited to mediating the hole injection problem. However, these materials are not ideal. The polymer devices have generally lagged behind the molecular-based devices, probably in part, because more intensive study and improvement of contacts has been pursued for the molecular materials.

Another source of trouble at the anode is that ITO may be degraded by extended operation in organic devices. It is thought that the compound decomposes and that In ions migrate into the organic layer (possibly accompanied by oxygen, which would cause damage as well). The In ions can be reduced to In metal as well with potential for developing localized shorting through the thin organic layers. This process is presumably driven electrochemically by the device bias voltage, as it occurs even in cases where the organic compound is known to be stable in contact with ITO under zero-bias conditions. Further evidence of an electrochemical source of the problem is found in the fact that coating the ITO with a conducting polymer such as polyaniline or polythiophene eliminates the decomposition. Presumably, the conducting polymer reduces the electric field present near the surface of the ITO and consequently eliminates the electrochemical driving force for decomposition.

9.6 DEFECTS IN ORGANIC MATERIALS

It may not be surprising that defects in organic materials are just as much of a problem as in inorganic materials. Upon further reflection, it may be surprising that defects are not completely prohibitive to the operation of organic devices. Defects in organic materials can be divided into primarily chemical and primarily structural defects. Chemical defects might be materials with incorrect functional group attachments. For example, if some of the side chains in MEH-PPV failed to form or were replaced by other species a local chemical defect would result. Likewise, a hydrolyzed or otherwise destroyed double bond would destroy the conjugation of the molecule. Organic synthesis inevitably results in local chemical defects of this type. It should not be surprising that such defects could trap carriers, bind excitons, block carrier and exciton motion, and encourage non-radiative exciton recombination. Chemical defects can be expected to increase over time due to the presence of excitons and other reactive sites on molecules. For example, a water molecule can be decomposed in the presence of an exciton on a -CH=CH- conjugated structure to yield a $-CH_2$-CHOH- single bonded structure. This is bond hydrolysis referred to above and is a major reason why water is a problem in organic electronic devices. We will not say more about chemical defects as they are simply the result of unintended chemical reactions and destroy the structures we were relying on to achieve a given behavior in the organic compound. Some chemical defects can be reduced or their formation prevented by more careful synthetic approaches with higher yields, approaches designed specifically to avoid particularly harmful results, better purification of the resulting materials, better removal of problem species such as O_2 and H_2O from the final device layers, and better seals to protect the finished structure from contamination by reactive species. Discussion of the effect of chemical defects may be found in many sources, for example in Nguyen or Grozema in the recommended readings.

A more subtle type of defect is a structural defect in an organic molecule. The more commonly recognized structural defects include crystalline defects when the organic material crystallizes, chain ends in polymers, particularly problematical geometries in which two molecules might meet or cross, and physical deformations. These defects are intrinsic regardless of the skill of the synthetic chemist, and cannot be as easily detected or eliminated.

For example, a simple bend in a conjugated molecule will affect the HOMO and LUMO states dramatically. Consider a conjugated organic molecule such as trans polyacetylene (Figure 9.1). If one of the single bonds is allowed to rotate through a moderate angle then it becomes immediately impossible to transfer the double bond to the site of that single bond, because the double bond requires a very specific orientation of the sp^2 hybrid orbitals (Figure 9.2). The presumption in the description of diffusion of carbocation and carbanion defects was that the local double bonding structure could be rearranged at will. Therefore a twist of any of the single bonds, which would be one way of bending trans polyacetylene would restrict movement of the carriers. Theoretical models of torsional deformation of conjugated organic molecules confirm this picture. Although charges can move through such a structure, their mobility is reduced.

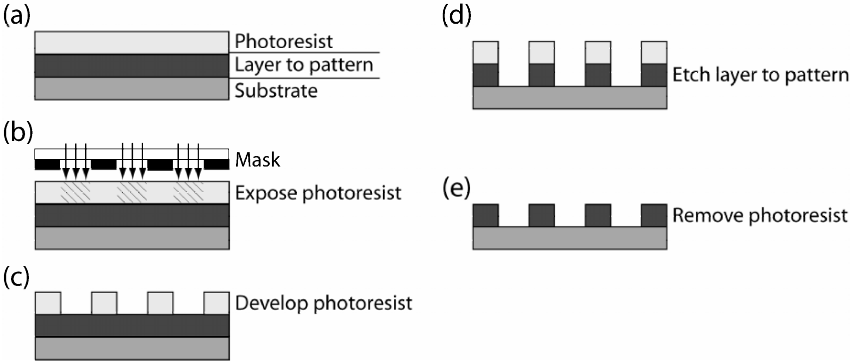

Figure 9.28: The basic steps in conventional photolithography. The approach begins with deposition of a photoresist material on the surface of a wafer coated with a layer to be patterned. This process is for a “positive” photoresist that increases its solubility when exposed to light (arrows) [step (b)]. The photoresist development step removes the exposed resist. The problem when patterning organic materials is step (e) in which the surface is typically exposed to an oxygen plasma that would remove both the photoresist and the organic layer to be patterned.

Returning to the LCAO discussion of Chapter 5, it is also hopefully apparent that any distortion of the geometry that would normally lead to an ideal bond will raise the energy of the bonding states and lower the energy of the antibonding states. Therefore, any bend in the backbone of a conjugated organic molecule must, by distorting the bonding patterns giving rise to the HOMO and LUMO states, reduce their energy difference locally. Therefore, a bend in a conjugated molecule, even if it does not involve a chemical defect, should bind excitons locally and reduce their energy. As we saw with inorganic materials, light emission is generally localized at such defects. Therefore, the only way to achieve the excitation properties of an ideal organic molecule is to assure that it never distorts. This is formally impossible to achieve for finite temperatures and can be made worse by structures that favor distortion of the molecules. Such distortions would also be natural in any non-crystalline material. Localized luminescence of organic molecules at bends in their structure has been observed by scanning probe techniques although whether the bends are caused by physical or chemical processes is not clear. The nature of physical and chemical defects is a matter of current debate and study. We will not say more here except to reiterate the essential point that **any physical or chemical distortion of an organic molecule will lead to a local trap for carriers or excitons and will degrade the optoelectronic properties.**

9.7 PATTERNING ORGANIC MATERIALS

Although this book does not consider lithography and other issues related to patterning of microelectronic materials in general, patterning organic materials is sufficiently distinct because of the problems involved that it deserves some mention. The patterning methods that have resulted have since been broadened to include application to other materials including conventional semiconductors.

The traditional method of patterning electronic materials, outlined schematically in Figure 9.28, begins by forming a uniform layer of the material across a substrate surface. This is then coated with a polymer known as a photoresist, generally by pouring it onto the wafer surface and spinning the wafer at a high speed. This results in a nice uniform photoresist coating across the substrate. The polymer is exposed to a pattern of light that either increases or decreases its solubility in some solvent. The higher solubility material is removed by the solvent, leaving the remainder behind. So far so good. To this point the process is compatible with organic materials. The next step is to remove the layer to be patterned which is not protected by the photoresist. Now comes the problem. The photoresist is typically an organic polymer. Therefore if the material to be patterned is also an organic polymer it is difficult to achieve a selective removal of the desired layer without also removing the photoresist. Even if one could do that the photoresist would remain as a coating on the protected parts of the layer to be patterned. In inorganic pattern generation the next step would be to expose the entire wafer to an oxygen plasma. Such a plasma very rapidly removes any organic material from the surface, leaving a nice clean patterned layer. Again, this is a problem when the layer of interest is itself a polymer. The problem of photoresist removal is an even greater problem than the selective etching of the layer to be patterned because the exposure process rendering the photoresist relatively insoluble makes it much more difficult to remove by design.

Various methods have been developed to deal with the problems with conventional lithography outlined above. Those described here are shown schematically in Figures 9.29 and 9.30. Some are adaptations to the traditional lithography approach that attempt to make it usable with a polymer underlayer. For example, one can insert a metal protective layer under the photoresist and use the photoresist to pattern the metal. That metal then acts as the mask for removal of the underlying organic material. Typically one can choose a metal that can be etched away at the end without affecting the underlying polymer that was to be patterned. This approach is cumbersome and if the metal is not sufficiently protective the underlying layer may be damaged during removal of the photoresist.

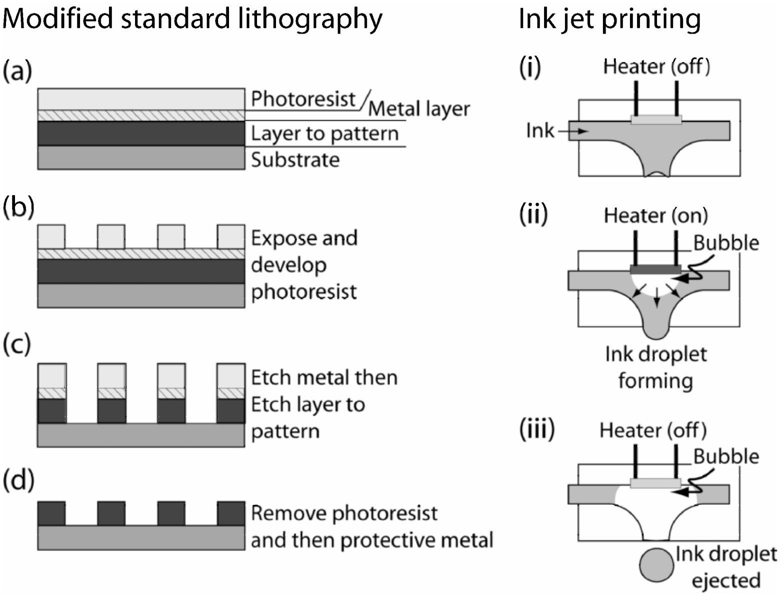

Figure 9.29: Two methods for conducting lithography on a material not compatible with conventional methods. Left: use of a metal layer to protect the material to be patterned from the process used to remove the photoresist. The protective metal is removed after the photoresist is removed. Otherwise the process is similar to that shown in Figure 9.28. Right: ink-jet printing has been used to print materials that can be dissolved or suspended to form an ink. The figure shows the operation of a print head. (i) Ink flows into the channel in the print head against the heater and opposite the print nozzle. (ii) The heater is turned on boiling the ink locally. The resulting bubble ejects a small droplet of ink (iii) and the heater is turned off, allowing the bubble to collapse and new ink to be drawn into the print head.

A second approach, which is attractive because it is a direct-write method, is to synthesize the material for the layer to be patterned in soluble form and then to dissolve it and write it directly onto the substrate in patterned form using an ink-jet printer [see, for examples, References 34-36]. These printers have remarkable resolution (patterns below 10 micron feature sizes can be achieved) and can directly write the material in question on the wafer without the need for subsequent patterning with a photoresist. This direct write approach means that no photomask is required and the pattern can be changed at any time by reprogramming the ink-jet printer. This method has been used for printing organic light emitting diodes devices with considerable success.

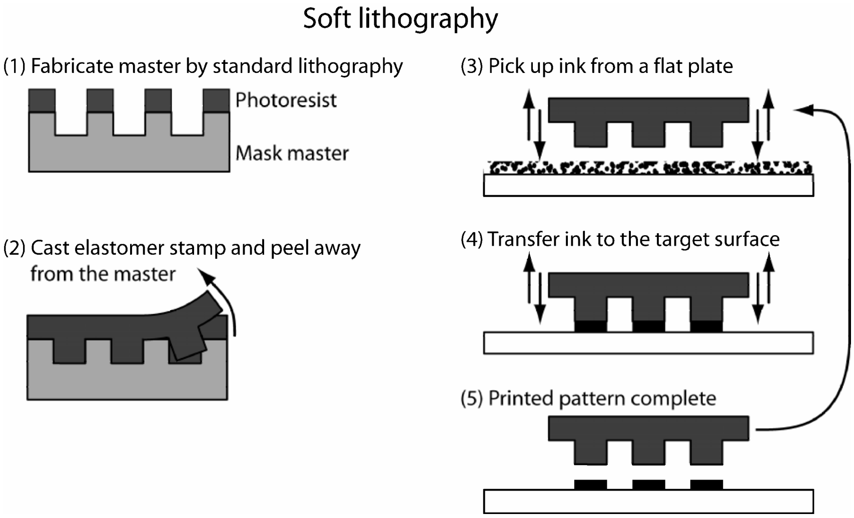

Figure 9.30: A schematic diagram of the basic steps in soft lithography. (1) A mask master is produced by standard lithography methods (see, for example Figure 9.28). (2) An elastomeric material such as polydimethylsiloxane is poured over the master and, with proper processing, covers the master conformally. The resulting stamp is peeled away from the master. The material to be printed, for example an ink, is picked up with the stamp (3) and transferred to the target surface (4). The ink should be designed to adhere well to the target and only weakly to the stamp so that the stamp comes away clean from the surface (5) leaving a complete and defect-free pattern. The stamp can be re-inked and used repeatedly.

The most dramatic improvement that is now being applied to patterning of a wide variety of materials from Si to polymers to metals is “soft lithography”, known also by various names other, the most intuitive of which is “micro contact printing”. A more detailed discussion and references may be found in Rogers and Nuzzo in the recommended readings. At its heart this is classical printing technology in which a raised pattern is produced on a stamp, the stamp is inked, and the ink is printed onto a surface. Amazingly, this process has been shown to be capable of printing even nanometer sized features, although the practical limit for the method is probably between 0.1 and 0.2 microns.

A typical process sequence for microcontact printing is shown in Figure 9.30. There are various implementations of this approach. We will consider a typical and relatively generic method here. The first step in the process is generally to create a master pattern in a hard material such as Si or quartz using conventional lithographic methods outlined above. For the highest resolution patterns it may be necessary to use electron-beam lithography. One then casts a layer of flexible rubbery polymer uniformly across the patterned master. A typical material used for this casting is polydimethylsiloxane (PDMS). The PDMS layer can then be peeled off of the master leaving a flexible polymer stamp containing the imprint of the master pattern. The remarkable aspect of this transfer is that the substrate pattern can be faithfully transferred to the PDMS even for nanometer feature sizes. It is useful for polymer lithography particularly because the only requirement is the ability to tailor the adhesion between the various layers that are put in contact with each other. It is not necessary to use an aggressive solvent or oxygen plasma to remove a polymer during this process.

The material to be printed is then transferred to the PDMS stamp by one of various methods. For example, a metal could be evaporated onto the PDMS stamp or a polymer or organic molecule could be applied to the stamp by precipitation from a solution. The simplest method is to deposit the ink on a flat plate and to pick up that ink on the stamp by simply pressing the stamp down on the surface. One then inverts the stamp and adheres the coating on the PDMS to a substrate of choice such as a Si wafer. The PDMS stamp is then peeled away, leaving the printed material on the substrate. To accomplish this it is necessary that the PDMS faithfully adopt the shape of the master, it must peel away from the master cleanly, it must pick up the ink effectively, and it must deposit that ink on the substrate. Of these the hardest to accomplish is the last. It is helpful if the ink will react strongly with the surface to form a strong bond and that the ink interact with the stamp only sufficiently to assure it is picked up initially. Specifically designed adhesion and release layers are commonly used, especially when transferring solid materials (see next) rather than inks.

Soft lithography is even more interesting because it can also transfer an active layer such as a thin single crystal of Si to any substrate surface desired. This is done by forming a brittle or soluble layer in the Si substrate at a fixed distance below the surface and below the active devices in the Si to be transferred. The stamp is attached to the active layer to be transferred and the detachment layer is used to remove the bulk of the substrate. The active devices are now attached to the stamp as in the printing process described above and can be transferred to another substrate. This has allowed creation of “flexible” Si electronic devices.

For more details on soft lithography the reader is referred to the recommended readings and references.

9.8 SUMMARY POINTS

- Organic devices are made from molecular (better performance) or polymer (more easily processed) materials. Molecular species have a single function normally and are blended when multiple behaviors are required. Polymers may be multifunctional based on copolymerized sections.
- Molecular species may be designed to have high crystallinity, leading to high carrier mobilities and good OTFT performances. Molecular materials have lower crystalline quality and lower mobility in general.
- Organic electronic materials are fully conjugated (they have a continuous double bond structure running through their structure). The π bonds associated with conjugated structures are rigid (they do not rotate). Conjugated molecules may conduct charges by breaking double bonds. Reconstitution of the broken bond may result in light emission.
- Any physical or chemical defect in an organic molecule will tend to lower carrier mobilities, trap charge carriers and excitons locally, will encourage non-radiative recombination, and will lower the energy of emitted photons in radiative processes. Many of these defects are intrinsic to the materials and many are more common for certain types of molecules or certain processing methods.
- Organic molecules may behave as indirect-gap semiconductors in that their minimum energy excitation may involve a change in physical structure. Transitions involving triplet states are forbidden. Only singlet states may recombine efficiently.
- Molecules having little conformational change associated with excitation are efficient light emitters.
- Coherence distances for defects on molecules are usually 1-2 nm. Conformational changes associated with excitations or defects are usually limited to this distance.
- Carbocations are positively-charged atoms and behave as do holes in inorganic materials and have higher mobilities in general than electrons (carbanions).
- Carbanions are negatively-charged atoms and behave as do electrons.
- Solitons are (for our purposes) uncharged dangling bond states (i.e. free radicals).
- Exciton binding energies in organic materials are generally high, 0.1-1 eV. They involve carbocation/carbanion pairs on adjacent C atoms.
- Limitations to OLED efficiency include: (1) imbalance in charge injection, (2) poor use of energy in triplet states, (3) low radiative recombination relative to non-radiative recombination, (4) problems with escape of the emitted light.
- Most molecules transmit electrons or holes better than the other charge and are know as electron transmitting (ETL) or hole transmitting (HTL) layers, respectively.

- Transmitted charges tend to be more dispersed across the structure of the molecule while poorly transmitted charges are localized and are associated with larger bonding changes.
- HTL and ETL molecules are designed (1) for optimized energies of their HOMO and LUMO orbitals to match with contacts (for charge injection) or to provide barriers to the propagation of a given charge (usually also the poorly transmitted charge), (2) for good stability, (3) for resistance to crystallization if used in OLED devices.
- Dye molecules are used to provide efficient luminescence at a prescribed photon energy (wavelength). Dye molecules should (1) trap free carbocations and carbanions, (2) localize resulting excitons on a single molecule, (3) allow the exciton to decay radiatively in a short time, (4) use energy in both singlet and triplet states, (5) dissolve well in the matrix, (6) have a narrow emission spectrum, and (7) be chemically stable.
- Optimal dye concentrations place the molecules at a separation of roughly the Förster radius (1-2 nm).
- Some molecules (especially those incorporating rare earth or transition metals) are efficient converters of excitons from triplet states to singlet states.
- Cathode contact issues include the reactivity of low work function metals and the formation of dipoles at the cathode/ETL interface that interfere with charge injection. Polar compounds may sometimes be inserted into the interface to cancel the dipole and improve injection efficiency.
- The major issue at the anode is the barrier to charge injection because high enough work function metals are not available. This is dealt with by using a cascade of materials with increasing HOMO binding energy (farther from the vacuum level). In addition, electrochemically-driven reaction and decomposition of the ITO transparent conductor can occur leading to loss of performance in the device. This can be reduced by adding a conducting polymer in the interface.

9.9 HOMEWORK

1) Sketch the structure of trans-polyacetylene containing a carbanion (the organic equivalent to an "electron") and a carbocation (hole) as separate solitons, not as an exciton pair in to configurations: (i) with both defects on one side of the chain and (ii) with the defects on opposite sides of the chain. Briefly explain why the structure is more stable with defects on opposite sides of the chain.

2) What is the purpose of Ir(ppy)$_3$ in an OLED and why is this important?

3) What is required for an organic molecule to be capable of transferring charge (i.e. transferring carbocations or carbanions) along its length?

4) It is possible to produce an OLED with a single layer of material (for example ppv) between two electrodes. Explain briefly:
   a) Why do the carriers (on average) not simply pass through the material to the other electrode? [There are two major factors in this behavior.]
   b) Why is this a diode? (Why is it so much harder to inject current in one direction than in the other?) You may wish to accompany your answer with a sketch of the band edges/Fermi energies in the device.

5) When designing a molecular material for use in
   a) an OLED (for example as a hole transporter), what is the advantage of choosing an asymmetric structure or one containing large side groups?
   b) a TFT (for example as the channel), what is the advantage of a small and highly symmetric molecule?

6) Why is Alq$_3$ a better electron transporter than a hole transporter?

7) What is the primary problem in application of hole transport layers and how does CuPc improve this situation?

8) What is the ideal concentration of dye molecules in an OLED emission layer and why are higher or lower concentrations less efficient?

9) What is the primary advantage of polymer over molecular organic materials in OLED's?

10) If the cathode contact to an electron transporter layer is a Schottky barrier type contact, why is there no observable depletion region in the organic material?

11) What are the major issues related to the anode and cathode contacts to OLED's and how have these been reduced in operational devices?

12) Why are dye molecules producing saturated colors important to designing a better full color display based on OLED's?

13) Consider the device structure shown in Figure 9.17. For each layer shown give the primary purpose of the layer and the most important aspect of its properties that contributes to achieving this purpose.

14) If the mobility of a carrier in an organic material is 0.001 $cm^2\ V^{-1}s^{-1}$ and the effective mass of an electron is the rest mass, m_0,

    a) calculate the approximate time between scattering events. [Hint: 1 $cm^2\ V^{-1}s^{-1} = 10^{-4}\ A\ s^2\ kg^{-1} = 10^{-4}\ C\ s\ kg^{-1}$.]
    b) if the device is biased to 8V and is 8 nm thick, estimate the average drift velocity of the carriers.
    c) Given the results of (a) and (b), estimate the average distance a carrier moves between scattering events.

9.10 SUGGESTED READINGS & REFERENCES:

Recommended readings:

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