CHAPTER 2 Theory and Review

2.1 Molecular Electronics

Conventional electronic materials are metals and semiconductors whose conductivities are in the range $1\text{-}10^{10}$ Scm^{-1} and 10^{-10} -1 Scm^{-1} respectively [1]. In contrast, most organic materials are insulators with conductivity in the range 10^{-14} -10^{-9} Scm^{-1}. However, this concept has changed in the last decade since the discovery of conducting organic materials such as donor-acceptor complexes, conjugated polymers and coordination compounds.

2.1.1 Donor-Acceptor Complexes

A donor-acceptor complex (DA) is made up of a compound with low ionization energy (electron donor) and a compound with high electron affinity (electron acceptor). According to Mulliken [2, 3] and Brackmann [4], the ground state of DA-complexes can be in neutral form with a minor contribution of an ionic resonance structure. The ionic character prevails in excited state when the material absorbs light (Equation 2.1).

$$\underbrace{(\underline{D\bullet\bullet\bullet\bullet A} \leftrightarrow D^{+}\bullet\bullet\bullet\bullet A^{-})}_{\text{Ground state}} \xrightarrow{h\nu_{CT}} \underbrace{(D\bullet\bullet\bullet\bullet A \leftrightarrow \underline{D^{+}\bullet\bullet\bullet\bullet A^{-}})}_{\text{Excited state}} \qquad 2.1$$

Due to optical excitation, an electron is transferred from the donor to the acceptor molecule. The corresponding charge-transfer absorption energy, $h\nu_{CT}$, is given by Equation 2.2 [5],

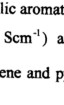
$$h\nu_{CT} = I_g - A_g - \frac{e^2}{r_{D^+A^-}} - \Delta W \qquad 2.2$$

where I_g is the donor ionization energy, A_g is acceptor electron affinity, $\frac{e^2}{r_{D^+A^-}}$ is the Coulomb energy of the $D^+ \bullet \bullet \bullet \bullet A^-$ ion pair with equilibrium distance $r_{D^+A^-}$, and ΔW is additional energy term which represents the mesomeric energy and various other energy terms.

Two groups of DA-complexes may be distinguished, namely weak molecular complexes (non-bonding type) and strong molecular complexes (dative type). The weak molecular complexes consist of donors with relatively large ionization energy ($I_g > 7.5$ eV) and acceptors with low electron affinity ($A_g \approx 0.7$-2.0 eV) [6]. According to Mulliken, only weak intermolecular electron transfer from D to A exists in the ground state. The conductivity of this type of DA-complexes is usually below 10^{-5} Scm^{-1} [7]. An example is sodium-anthracene complex whose conductivity is 10^{-9} Scm^{-1} [8, 9, 10, 11]. The structure of anthracene is shown in Figure 2.1a.

The strong molecular complexes consists of very strong electron donors ($I_g < 7.0$ eV) such as aromatic diamines and acceptors with high electron affinity. They display a considerable electron transfer from the donor to the acceptor even in ground state, which is no longer in consistent with the Mulliken model. The conductivity of this type of DA complexes is higher than 10^{-5} Scm^{-1}. Examples are DA-complexes consisting of polycyclic aromatic hydrocarbons with iodine or bromine such as perylene-bromine (1.2×10^{-1} Scm^{-1}) and pyranthrene-iodine (4×10^{-2} Scm^{-1}) [12, 13, 14]. The structures of perylene and pyranthrene are shown in Figure 2.1 (b) and (c) respectively.

(a)



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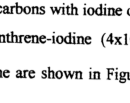
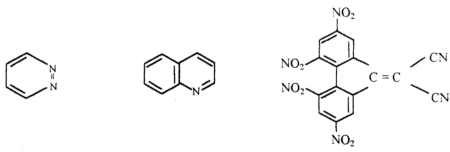


(c)

Figure 2.1 Structures of (a) anthracene, (b) perylene and (c) pyranthrene

The conductivity of DA complexes consisting of N-containing heterocycles donor range from 1 to 10^{-14} Scm^{-1}. Examples are pyridazine-iodine complex ($2x10^{-2}$ Scm^{-1}) [15], and quinoline-dicyanomethylene-9-polynitrofluorene complex ($5x10^{-5}$ Scm^{-1}) [16]. The structures of pyridazine, quinoline and dicyanomethylene-9-polynitrofluorene are shown in Figure 2.2.



(a) (b) (c)

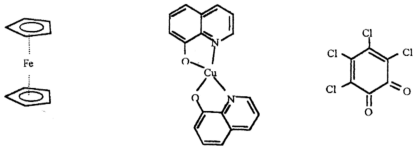
Figure 2.2 Structures of (a) pyridazine, (b) quinoline and (c) dicyanomethylene-9-polynitrofluorene

Organometallic compounds forming DA complexes with electron acceptors also shows intermolecular charge transfer (CT) bands [17]. The magnitude of the dark conductivity of these complexes depends on whether the ground state is of dative or non-bonding type.

Examples of the dative type are complex of ferrocene with tetrachloro-p-diphenoquinone [18] and bisfulvalenediiron-TCNQ complexes [19]. The conductivities of these complexes are $4x10^{-2}$ Scm^{-1} and 10 Scm^{-1} respectively. The structures of ferrocene is shown in Figure 2.3 (a).

The non-bonding type comprises the π complexes of Pd^{2+}–8–hydroxyquinolinate or Cu^{2+}-8-hydroxyquinolinate with o-chloranil [20]. The

conductivity of these complexes are approximately 10^{-12} Scm^{-1}. The structures of Cu^{2+}-8-hydroxyquinolinate and o-chloranil are shown in Figure 2.3 (b) and (c) respectively. Since Cu^{2+} is more easily reduced than Pd^{2+}, it can be concluded that a smaller fraction of $Cu^{2+}(Ox)_2$ acts as an electron trap. At higher concentrations, however, because of the adjacent position of Pd^{2+} and Cu^{2+} complexes, the recombination of electrons at the $Cu^{2+}(Ox)_2^-$ and holes at the $Pd^{2+}(Ox)_2^+$ is favoured and thus conductivity is reduced.



(a) (b) (c)

Figure 2.3 Structures of (a) ferrocene, (b) Cu^{2+}-8-hydroxyquinolinate and (c) o-chloranil

2.1.2 Conjugated Polymers

Conjugated polymers possess alternate single and double bond along the polymer chain. The pi-electron (π) system delocalized along the chain can support excited electronic states. These properties allow the polymers to exist in a wide range of oxidized and reduced states making them a useful semiconducting material. They have been intensively studied because of the high metal-like electric conductivity after doping compared to conventional polymers, which are insulators.

Conjugated polymer first reported in the late 1970's was polyacetylene (PA). Pure polyacetylene is a semiconductor whose conductivity is in the range of 10^{-12} - 10^{-6} Scm^{-1} [1]. It can be doped with chlorine, bromine, iodine or arsenic

pentafluoride (AsF_5). This increases its conductivity by several orders of magnitude. Structure of PA is shown in Figure 2.4.

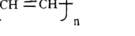


Figure 2.4 Structure of polyacetylene

Ideally, polyacetylene can be described as a one-dimensional semiconductor capable of supporting charge carriers which can migrate through the chain. Thus PA has the potential to display highly anisotropic properties. It was first synthesized by Natta, Mazzanti and Corradini in 1958 [22]. Since the discovery that PA became conducting after treatments with oxidizing or reducing agents [21], a new class of conducting conjugated polymers had been reported such as polyphenylene (PPP), polyaniline (PANI) and polypyrrole (PPY).

PANI was first investigated by MacDiarmid and co-workers in 1986-1987 [23]. It is a most promising conducting polymers due to its chemical and oxidative stability in both pure and doped forms [1]. The structure of PANI shown in Figure 2.5 consists of alternating reduced and oxidized repeating units. PANI is an insulator with conductivity of approximately 10^{-10} Scm^{-1}. When modified by the applied acid, the conductivity may increase up to the order of $1-10$ Scm^{-1}.

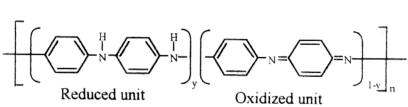


Figure 2.5 Structure of polyaniline

PPY was a conductive polymer first discovered in 1968. Dall' Olio et al. prepared it by the anodic oxidation of pyrrole in sulfuric acid [24]. PPY is easily synthesized, environmentally stable and possess good electrical and mechanical properties. Conductivity for pure PPY is 40 Scm^{-1} while that of doped PPY is about 10^2 Scm^{-1} [25, 26]. The ideal conducting structure of PPY consist of one-dimensional chain made up of identical monomer as shown in Figure 2.6. For conducting purpose, the π electron in each monomer become delocalized over the length of the polymer chain in the form of bands due to the significant overlap integral.

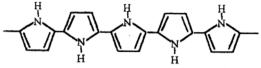


Figure 2.6 Structure of polypyrrole

2.1.3 Coordination Compounds

Coordination compounds consist of a central transition metal ion surrounded by a set of other atoms, ions or small molecules called ligands. The resulting compound is called a complex or a complex ion, if it is charged [27].

For conducting purposes, the central metal ion should stack one above another to form a columnar structure forming a polymer. An example is $Cs_2[Pt(CN)_4]Cl_{0.3}$ which has a conductivity of $200\,Scm^{-1}$. It is also a 1-D metallic complex. The structure of $[Pt(CN)_4]^{X-}$ ion is shown in Figure 2.7. The molecules are arranged along one direction with a short inter-molecular orbital overlap with the neighbouring molecules in this direction. Electron transport can arise from the existence of a partially filled band or from reduced coulombic interactions which will allow easy electron transport between localized centers along the conducting axis.

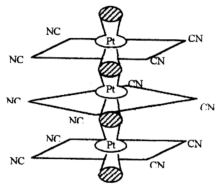


Figure 2.7 Columnar stacked structure of $[Pt(CN)_4]^{X-}$ showing the overlap of platinum $5d_{z^2}$ orbitals

2.2 Theory of Electronic Conduction in Molecular Electronics

Two requirements must be fulfilled for direct conduction (dc) to exist. Firstly, free carriers must enter the system; and secondly, these carriers which have entered the system must in some way transfer their charges to the other contact so as to leave it again. The band model used for inorganic semiconductors is fundamentally inapplicable to organic solids because coherent transfer in conduction band in organic solid is likely to be narrow. There are several mechanisms for the transfer of carriers from one contact to the other [28].

a) *Auto-ionization model.* This model proposes that one-photon absorption gives rise to a state which either degrades or else forms an ion-pair which is then separated into two oppositely charged species under the combined action of thermal energy and electric field.

b) *Phonon assisted hopping model.* This model involves hopping over the potential barrier separating two adjacent molecular, or ionic sites. This causes a drift velocity component in the direction of the applied field.

c) *Quantum mechanical tunneling model through the potential barrier.* The transition takes place between exactly matching energy levels on either side of the barrier.

d) *Long or variable range hopping or percolation model.* It means that non-coherent charge transfer between non-adjacent molecular or ionic sites. This replaces the sharp energy band edges by slowly decaying tails extending well into the energy gap and arising from the very disorder characterizing amorphous systems.

e) *Exciton model.* In this model, charge carrier is not transferred by the free charge carrier as such but rather its energy in the form of an exciton to be dissociated at

the carrier exit electrode so as to yield again a free carrier which can enter the external circuit.

Generally, two common models has been used to explain the dark conduction in molecular electronic. They are tunneling and hopping models.

2.2.1 Tunneling Model

This model is first discussed by Eley et al [29]. A quantum mechanical tunneling model was suggested to explain how a π electron can move from one molecule to a neighbouring molecule in a typical molecular crystal. The charge carriers would tunnel to the adjacent molecule in two stages. First, an electron produced through the excitation of a single molecule, either thermally or optically, to a normally unoccupied first excited π-orbital and a hole produced in highest occupied molecular orbital (HOMO) which normally contain two π electrons. The excited state of a molecule can be either a singlet or a triplet and the energy depends on the spin. The excited electron then tunnels through the intermolecular barrier to the adjacent molecule. The hole tunneling is equivalent to the electron tunneling in the opposite direction (Figure 2.8). The electron may return to its ground state, but the probability is much lower than tunneling to its neighbour molecule. This model can explain the order of magnitude of the mobility, the compensation law and the anisotropy of conductivity. However, this model was unable to explain the difference in the electron and hole mobilities.

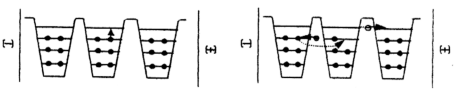


Figure 2.8 Conduction by tunneling model

2.2.2 Hopping Model

Hopping conduction is the dominant electrical conduction mechanism for materials with high resistance. Typical resistance between neighbouring impurities become larger than those connecting some remote impurities whose energy levels happen to be very close to the Fermi level. The mechanism is named variable-range hopping (VRH) because the characteristic hopping length increases with lowering temperature. It is known as Mott's law for a constant density of states. A hopping model is shown in Figure 2.9 [30]. An electron would be produced through excitation of a single molecule either thermally or optically to a normally unoccupied first excited π-orbital. The electron then hops across the potential barrier. The electron hopping in one direction is equivalent to the hole hopping in the opposite direction.

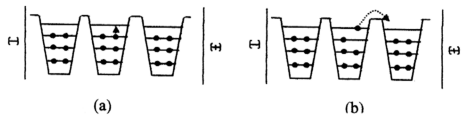


Figure 2.9 Conduction by hopping model

According to Mott's law, hopping conduction occurs in the states whose energies are concentrated in a narrow band near the Fermi level. The temperature dependence of the dc conductivity exhibits universal behavior [31] [32]

$$\sigma = \frac{3e^2 \upsilon_o}{128\alpha^2}\left(\frac{T_o}{T}\right)^{\frac{1}{2}} N(E_F)\exp\left[-\left(\frac{T}{T_o}\right)^{-\frac{1}{4}}\right] \qquad 2.3$$

18. E. Adam, M. Rosenblum, S. Sullivan and T. N. Margulis, *J. Amer. Chem. Soc.*, **89,** 4050, (1967)

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process will increase the conductivity of organic polymers to several order of magnitude.

Doped organic polymers are actually very different from the usual doped inorganic semiconductors such as GaAs, Si, or Ge [42, 43], and this is not because of the larger doping levels achieved in doped polymers but because polymers possess highly anisotropic interaction which result in low dimensionality of electronic motion and can lead to collective instabilities typical of quasi-one-dimensional materials, such as Peierls-Frölich modes. In addition, the electronic excitations or charge transfer processes markedly affect the atomic geometry in organic polymers, just as in typical organic molecules.

Basically, doping may produce either an increase in the carrier concentration or in the carrier mobility, or even both. Flash photoconductivity experiments show that the increase in the carrier concentration predominates in organic solid whereas the mobility is independent of the dopant levels over a 100-fold concentration range. Further prove was provided by measurements on the metal-free phthalocyanine doped with acceptors such as tetracyanoethylene (TCNE), TCNQ or chloranil.

2.3 Fourier Transform Infrared Spectroscopy

Infrared (IR) radiation refers to the portion of the electromagnetic spectrum between microwave (10^5-10^3 cm^{-1}) and the visible regions ($2.5x10^4$-$1.4x10^4$ cm^{-1}) [44]. For infrared spectroscopy, the most important region is between wavenumber 4000 cm^{-1} and 400 cm^{-1}. Wavenumber is proportional to energy and is defined as the inverse of the wavelength.

Typically, translation, rotation and vibration are the three types of motion for a molecule. Infrared absorption is normally associated with changes in vibrational and rotational levels in a molecule. Molecular vibrations are either stretching or bending.

Stretching vibrations can be either symmetric or asymmetric (Figure 2.10). Bending vibrations (Figure 2.11) are rocking, scissoring, twisting, or wagging (Figure 2.11) depending upon the motion of the outer nuclei in comparison to the central nucleus. From Figure 2.11, the angle that are altered during the vibrations are labeled A. The dashed arrows during twisting and wagging represent motion behind the plane of the page and the solid arrows represent motion in front of the plane of the page. The numbers represent the orders in which the motions occur. Each of the motions has its own natural vibrational frequency. Normally stretching vibrations have higher frequency than bending vibration [45].

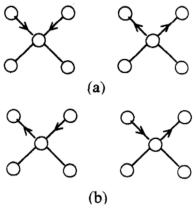

Figure 2.10 Example of (a) symmetric and (b) asymmetric stretching

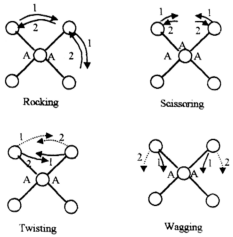

Figure 2.11 Examples of different bending vibration

When the incident frequency imposes on the molecule coincide with the natural frequency of the molecule, a transition from one vibrational state to another in the electronic ground state occurs. If this change is accompanied by a change in dipole moment, the vibration may be infrared-active. The infrared spectrum will show a peak caused by the absorption. Magnitude of the dipole moment transition will affect the intensity of the absorption [45]. For example, a molecule with permanent dipole moment absorbs strongly to give intense band. In contrast, symmetrical molecules absorb weakly to give either very weak band or no band at all.

Wavenumber of the absorption depends on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms as shown in Equation 2.8 [46].

$$\bar{\upsilon} = \frac{1}{2\pi c}\left[\frac{f}{(M_x M_y)/(M_x + M_y)}\right]^{\frac{1}{2}} \qquad 2.8$$

where $\bar{\upsilon}$ = wavenumber (cm^{-1})

c = velocity of light (cm/s)

f = force constant of bond (dyne/cm)

M_x= mass of atom X

M_y= mass of atom Y

For single, double and triple bonds, the value of the force constant are approximately $5x10^5$, $10x10^5$ and $15x10^5$ dyne/cm respectively. Due to the environmental factor, the calculated results are not highly accurate when compared to those obtained from the spectra.

A few basic requirements have to be met before a spectrum is interpreted. First, the resolution and the intensity of the spectrum must be high enough. Second, a reasonably pure compound should be obtained. Third, proper calibration should be

made so that each band corresponds to their correct frequency. Fourth, the medium of the sample should be taken into consideration so that bands due to the medium are deducted.

Basically, two important regions for preliminary examination are 4000 - 1300 cm^{-1} and 900 - 650 cm^{-1}. This is because many of the important functional groups such as $-NH_2$, -OH and -COO are in this range. For example $-NH_2$ bonds (primary amines) give two moderately intense stretching bands which corresponds to the asymmetrical and symmetrical N-H stretching vibrations. The two bands appear as doublet at 3350 cm^{-1} and 3180 cm^{-1}. For -OH, strong absorption for stretching vibration is expected in the region 3650 - 3584 cm^{-1}. If there is intermolecular H-bonding, the band will be broad and it could probably veil the appearance of other bands.

For an aromatic compound, absorption bands are expected for C-H and C=C. There are two characteristic C=C stretching absorption bands for asymmetric and symmetric bands near 1600 - 1585 cm^{-1} and 1500 - 1400 cm^{-1} respectively. The skeletal bands frequently appear as doublets, depending on the nature of the rings substituents. For example, mono-substituted aromatic ring showed bands near 750 cm^{-1} and 695 cm^{-1}, di-substitution can be divided into *ortho, meta* and *para*. Ortho-substitution shows bands at 750 - 760 cm^{-1}. Meta-substitution at 690 - 710 cm^{-1}, 770 - 780 cm^{-1}, and 810 - 820 cm^{-1}. Para-substitution at 810 - 820 cm^{-1} [45].

For carboxyl ion, COO^-, the C-O stretching bands appear at 1415 cm^{-1} and 1570 cm^{-1}. The bidentate bridging characteristic will cause the band frequency to shift to higher value. Similar case was observed in metal acetate [27] where a higher frequency band is observed when one of the C-O bonds have enhanced double bond character.

The region between 1300-900 cm^{-1} are referred to as the "finger print" region [46]. This region is unique for a particular molecule and is used as structural identification and confirmation.

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