Chapter 5

Nature of Charge Carriers in Disordered Organic Molecular Semiconductors

5.1 Introduction

Since the discovery of "plastic" based transistor[37, 49] and light emitting devices[1, 2, 6], organic molecular semiconductors(OMS) are being widely investigated. As already mentioned, OMSs belong to wide class of amorphous materials, known as disorder organic molecular solid(DMOS). These materials are composed of different types organic molecules starting from very small molecules to very large biomolecules like proteins and DNA, held together loosely by weak van der Waals type intermolecular force. The absence of long range order in these materials leads to the localization of the electronic wave function and results transport of charge carrier via thermally activated hops with carrier mobility $\mu$ as a strong function of temperature $T$ and electric field $F$ following a universally observed[11] Poole-Frenkel(PF) behavior

$$\mu(F, T) = \mu(0, T) \exp \left[ \gamma(T) \sqrt{F} \right]$$  \hspace{1cm} (5.1)

where $\mu(0, T)$ is the temperature dependent zero field mobility and $\gamma(T)$ is field activation of the mobility and recently, in light of theoretical studies[12, 13, 100] we have shown[48]
another important feature i.e. (iv) charge carriers are spatially correlated in these materials. Inspite of phenomenal progress in the field of organic molecules based electronics in recent years, there is still a lots of understanding concerning the certain fundamental issues in charge carrier transport in these materials, for example, considerable debate[11, 81, 82] is going on the fundamental question like, what is the nature of charge carriers in DOMS? Though, this issue has been settled in ordered molecular organic materials[101, 102, 103] and shown that the strong electron-phonon interaction explain the experimental data consistently but this issue in DOMS is being debated for quite some time. Answer to this question will be a key input for understanding the charge transport mechanism and the development of new materials and new devices based on these materials. An indication of the difficulty in finding the nature of charge carriers and understanding the transport processes in these materials is evidenced by the conflicting viewpoints. At present, there are three viewpoints on the nature of charge carriers, which are (i) dressed electrons (known as polarons) due to strong electron-phonon interaction and the temperature dependence of the \( \mu \) arises due to polaron binding energy; (ii) bare electrons and temperature dependence of \( \mu \) is due to energetic and spatial disorder[104] and (iii) third viewpoint[13, 105] is the combination of these two opposite viewpoints and the charge carriers are polarons moving in disorder and the temperature dependence of \( \mu \) is due to both static disorder and polaron binding energy. It has been shown[13, 106] that polaron based models result unacceptable values of polaron binding energy and strong nearest neighbor intermolecular coupling if disorder is not included. As mentioned earlier, the intermolecular coupling in these DOMS is very weak and can’t account for strong nearest neighbor coupling. If it is assumed that energetic and spatial disorder are responsible for thermal activation of \( \mu \) and bare electrons, not polarons, are responsible for charge carrier transport, the probability of hopping is drastically reduced and again unreasonably strong intermolecular coupling is required to explain the experimental data. Here, we show that there is a natural solution to this apparent paradox and polaron is the
nature of charge carriers, emphasizing the important role of both disorder and electron-phonon interaction on the charge carrier transport in these disordered materials.

For our study we have chosen metal phthalocyanine (MePc) based thin films as the organic semiconductors because beside their potential application\cite{34, 37} for "plastic" based optoelectronic devices and transistor, these materials are (i) the most chemically and thermally stable compounds, (ii) suitable for organic single layer structures with different metal electrodes without effecting the interface properties and finally (iii) reproducibility of experimental data for devices with MePc as active organic layers, which is a major problem with most other organic materials\cite{38, 39, 40} due to their degradation with time and the interaction of organic materials with the different metal electrodes.

5.2 Experimental Details

MePc based organic single layer devices were prepared by sandwiching a thin active organic layer of MePc between Indium Tin Oxide (ITO) coated glass substrate and thermally evaporated metal electrodes, using vacuum deposition technique (VDT) (Appendix-C). Details about the device fabrication are discussed in Chapter-II. We report the experimental investigation on charge carrier transport in hole only devices based on metal/MePc/metal structures. Indium tin oxide (ITO) has work function (4.75 eV) very close to the ionization potential (4.8 eV) of MePc\cite{34}, hence the ITO/MePc interface behaves an Ohmic contact. The temperature dependent current-voltage (J-V) characteristics were studied for ITO/MePc/Al structures with different thicknesses of MePc layers. Here ITO is chosen to be the anode. By properly choosing contacting metals (Cu and Al), current injection and transport due to holes have been investigated.
5.3 Polaron Hopping in OMS

As discussed in previous chapter, there are basically three models to explain the charge carrier transport in these materials. In a very first approach, Gill\cite{45J} attempted to describe the universally observed thermally activated and PF behavior of $\mu$ using a phenomenological non-Gaussian disorder model(NGDM). The temperature dependence of the zero field mobility can be given by(from Eq.4.7 in Chapter-IV),

$$\mu(T, F \rightarrow 0) = \mu_0 \exp \left( - \frac{\Delta}{k_B T} \right)$$

where $\Delta$ is the temperature independent activation energy and $\mu_0$ is the temperature independent zero field mobility. This model has been criticized\cite{12, 46, 48} for lacking a first principle explanation of PF behavior of $\mu$ and non-inclusion of another universal feature i.e. the Gaussian distribution of energy levels, $g(E) \propto \exp(-E^2/4\sigma^2)$, where $\sigma$ is the r.m.s deviation of hopping site energies.

Bassler proposed\cite{46} the uncorrelated Gaussian disorder model(UGDM), which describes the carrier transport as a biased random walk among the dopant molecules with Gaussian-distributed random site energies. Although UGDM explains some features of experimental data and provides support for PF behavior of carrier mobility, several discrepancies\cite{48} emerge with uncorrelated description of Gaussian disorder model, which is discussed in Chapter-IV. Garstein and Conwell\cite{47} first showed that a spatially correlated potential is required for the description of PF behavior of mobility and subsequently Novikov et al.\cite{12} have proposed a correlated Gaussian disorder model(CGDM) to describe the charge carrier transport in these materials.

In the previous chapter, we have shown\cite{48} that the CGDM successfully explains the experimental data emphasizing, whatever be the nature of charge carriers, charge transport occurs by correlated hopping among the molecular sites with GDOS of highest occupied molecular orbital(HOMO) and/or lowest unoccupied molecular orbital(LUMO) in these dis-
ordered materials. In case of both Gaussian disorder models (UGDM and CGDM), the temperature dependence of zero field mobility is given by (from Eq. 4.9 and 4.13 in Chapter IV)

\[ \mu(T,F \to 0) = \mu_0 \exp \left[ \frac{-A\sigma^2}{k_B T^2} \right] \]  

where \( A = 2/3 \) in UGDM \( [46] \) and \( 3/5 \) in CGDM \( [12] \).

The Arrhenius plots result an apparent activation energy \( E_a \), which is given by

\[ E_a = -k_B \left\{ \frac{d(\ln \mu)}{d(1/T)} \right\} \]  

Hence \( E_a = \Delta \) in NGDM \( [45] \) and \( E_a = B \sigma^2 / k_B T \), in case of Gaussian disorder models and \( B = 8/9k_B \) in UGDM \( [46] \) and \( 18/25k_B \) in CGDM \( [12] \). If we take the contributions both from the polaron binding energy \( E_{pol} \), and from the static disorder \( E_{dis} \), \( E_a \) should be

\[ E_a = E_{pol} + E_{dis} \]

Fig. 5.1 shows the temperature dependence of zero field mobility and it is clear that both
Figure 5.2: Theoretical fit to temperature dependence of zero field mobility in CuPc for two different thicknesses using Gaussian distribution of activation energy, which is shown in inset.

\( \ln(\mu(0,T)) \) vs. \( \frac{1}{T} \) and \( \ln(\mu(0,T)) \) vs. \( \frac{1}{T^2} \) result nonlinear Arrhenius plots and it is impossible to distinguish between \( E_{pol} \) and \( E_{dis} \) and their respective values from \( E_c \). Here, we show that the interplay between these two contributions on the carrier transport can be explored by studying the temperature dependence of \( \mu \) over extended range of temperature and measuring at least one contribution in \( E_c \), independently. It is clear from Fig.5.1 (more detailed discussion is given in Chapter-IV) that both, NGDM and UGDM or CGDM agree well with experimental data in higher temperature region \( (T \geq 140K) \) and gradual change in slope in the Arrhenius plots can be explained either by invoking the distribution of \( E_c \) or by distribution of \( \sigma \), but the underlying assumption behind the second proposition is hard to justify. We have found that the Gaussian distribution of \( E_c \), which is

\[
\phi(E_c) = A \exp \left\{ -\frac{(E_c - E_{c0})^2}{4\sigma_c^2} \right\}
\]

(5.6)
Figure 5.3: Absorption spectra of CuPc for two different thicknesses at room temperature. The spectral characteristics and width of the spectra do not depend on the thickness of the sample.

where $A$ is a normalization constant and

$$
\mu(0,T) = \mu_0 \int_0^\infty \phi(E_c) \exp \left( -\frac{E_c}{k_BT} \right) dE_c \tag{5.7}
$$

explain the data excellently, as shown in Fig.5.2. $E_c$, which is the maximum activation energy and $\sigma_c$, are the center and width of the Gaussian distribution and found to be 540meV and 80meV, respectively.

In this case, the temperature dependence of mobility follows $ln(\mu) \propto 1/k_BT$ instead of $ln(\mu) \propto 1/(k_BT)^2$ according to CGDM[12]. The spatial correlation in CGDM[12] has been shown to be resulted from the long-range interaction between charge carriers and permanent dipole moments of doped molecules in polymers and/or host molecules. However, it has been pointed out[100] that the mechanism responsible for PF behavior in different conjugated polymers and molecules cannot be due to charge-dipole interaction, because the PF behavior of $\mu$ has been universally observed in several doped and undoped organic semiconductors.
Figure 5.4: The hopping sites and hopping processes inside the intrinsic density of states of disordered molecular semiconductors.

Based on polymers or molecules with or without dipole moment. Recently, Yu et al.[100] have shown using first principle quantum chemical calculation that the thermal fluctuations in the molecular geometry can lead to spatial correlation through intermolecular restoring force and different temperature dependence in this case arises due to the fact that energetic disorder is temperature independent in CGDM, whereas it increases with temperature in molecular geometry fluctuation model[100, 107] resulting \( \ln(\mu) \propto 1/k_B T \) temperature dependence. We have used highly symmetric molecules with negligible dipole moment for our investigations and we find it hard to justify strong long-range charge-dipole interaction to be the origin of spatial correlation.

Fig.5.3 shows the absorption spectra of CuPc. The characteristic two-humped spectra are known as Q-band[34] in CuPc. The absorption co-efficient \( \alpha(E) \) for a given photon energy \( E \) is proportional to the probability \( P_{if} \) for the transition from initial state \( i \) (in HOMO) to the final state \( f \) (in LUMO) and the density of the initial and final state and given by, \( \alpha(E) \propto \Sigma P_{if} \rho_i \rho_f \), where \( \rho_i \) and \( \rho_f \) are the density of states in HOMO and LUMO of CuPc, respectively. There are two important parameters involved in the absorption spectra. First
is the center of the peak at around 2eV, which is the energetic separation between maxima of HOMO and LUMO and second is the full width at half maximum of about 460meV, which should be the maximum energetic separation between two hopping sites within the intrinsic GDOS, as shown schematically in Fig.5.4. Hence, the maximum contribution in the activation energy from static disorder will be around 460meV. We have also found that the 540meV is the maximum activation energy ($E_{a0}$), which has both contributions from static disorder and polaron binding energy. Combining these two electrical and optical measurements, we found 80 meV ($=540-460$meV) is the polaron binding energy. If we include the lower and upper limits of activation energy due to static disorder, which are 500meV and 580meV respectively, the polaron binding energy varies between 40 to 120meV. These observations are consistent with the third viewpoint i.e. disordered polaron moving in a correlated energy landscape is responsible for charge transport in disordered organic molecular semiconductors. These experimental findings settle an extremely important issue regarding the nature of charge carriers and have shown conclusively that polarons moving among static disorders are responsible for charge carrier transport in these DOMS.

5.4 summary

We have presented the first experimental proof that polarons are the charge carriers in molecular semiconductor using very simple experiments. These experimental findings resolve the internal inconsistency and settle an extremely important issue regarding the nature of charge carriers in disorder molecular semiconductors.