CHARGE TRANSPORT IN ORGANIC MULTI-LAYER DEVICES UNDER ELECTRIC AND OPTICAL FIELDS

DISSERTATION

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Charge transport in small organic molecules and conjugated conducting polymers under electric or optical fields is studied by using field effect transistors and photovoltaic cells with multiple thin layers. With these devices, current under electric field, photo-current under optical field, and luminescence of optical materials are measured to characterize organic and polymeric materials.

For electric transport studies, poly(3,4-ethylenedioxythiophene) doped by polystyrenesulfonic acid is used, which is conductive with conductivity of approximately 25 S/cm. Despite their high conductance, field effect transistors based on the films are successfully built and characterized by monitoring modulations of drain current by gate voltage and IV characteristic curves. Due to very thin insulating layers of poly(vinylphenol), the transistors are relatively fast under small gate voltage variation although heavy ions are involved in charge transport. In IV characteristic curves, saturation effects can be observed. Analysis using conventional field effect transistor model indicates high mobility of charge carriers, 10 cm²/V·sec, which is not consistent with the mobility of the conducting polymer. It is proposed that the effect of a small density of ions injected via polymer dielectric upon application of gate voltage and the ion compensation of key hopping sites accounts for the operation of the field effect transistors.
For the studies of transport under optical field, photovoltaic cells with 3 different dendrons, which are efficient to harvest photo-excited electrons, are used. These dendrons consist of two electron-donors (tetraphenylporphyrin) and one electron-accepter (naphthalenediimide). Steady-state fluorescence measurements show that inter-molecular interaction is dominant in solid dendron film, although intra-molecular interaction is still present. Intra-molecular interaction is suggested by different fluorescence lifetimes between solutions of donor and dendrons. This intra-molecular interaction has two processes, transport via \( \pi \)-stackings and transport via linking functional groups in the dendrons.

IV characteristic spectra of the photovoltaic cells suggest that the transport route of photo-excited charges depends on wavelength of incident light on the cells. For excitation by the Soret band and the lowest Q band, a photo-excited electron can transport directly to a neighbor dendron. For excitation by high-energy Q bands, a photo-excited electron transports via the electron-accepters.
To my parents
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CHAPTER 1

INTRODUCTION

1.1 Background of this thesis

Organic materials have a long history for human uses. A large fraction of material around our lives is made from organics in both small molecular forms and polymeric forms. For scientific or engineering fields, one of the oldest applications is to use dyes, which are still used extensively for researching and developing organic/polymeric photonic devices such as light emitting devices and photovoltaic devices.

In the era of woods and metals before late 19th century, artificial plastic materials were not yet developed. After first synthesis of plastic material, Bakelite by Leo Baekeland in 1907, subsequent developments of polymers such as Nylon and polyethylene improved basic demands for our living, such as clothes, small mechanical structures, and so on. This was in the area of chemistry and chemical engineering how to synthesize appropriate organics and polymers for those purposes. However, discovery of conducting polymers makes plastic materials one of popular topics in physics and its related area [1]. Many theories were developed to explain these unconventional materials and they were successful [2]. In addition, small molecules like pentacene and copper phthalocyanine (CuPc) have been widely used for electronic
Figure 1.1: Solar spectra of AM0, AM1.5 global, and AM1.5 direct (0.5 degree) + circumsolar (5 degrees) from the American Society for Testing and Materials (ASTM) (from Ref. [6]).

devices [3]. Electric devices such as field effect transistor or non-volatile memory using organic or polymeric materials [4, 5] are examples of applying these materials.

Another research topic in this field is to develop photonic organic materials for light emitting devices and photovoltaic cells. These two topics are now important in academy and industry because it is believed that organic or polymeric photonic application provides more versatility of device application, energy saving, and energy generation. Recently, development of solar cells with organics and polymers is also one of fast growing area due to expectation of energy shortage in the future [7, 8].
Organic or polymeric materials have a drawback, which is high bandgap energy, typically higher than 2.0 eV (approximately 630nm wavelength). Thus, these materials cannot absorb near infrared light from the Sun, whose energy spectrum is shown in Figure 1.1 [6]. But many organic and polymeric materials have multiple electronic bands to absorb a wider range of the solar spectrum and there are many possibilities to select bandgap energy for photovoltaic application.

Efficiency of organic/polymeric photovoltaic cell (about 10.4 % for dye sensitized photovoltaic cell [9], 3.0 % for organic polymer with fullerene [10] by Sharp Corporation) is still lower than inorganic based photovoltaic cell (approximately 30 % from GaInP/GaAs based photovoltaic cells [11]) [12], but it is getting close to typical efficiency of 15 % for commercial applications.
1.2 Topics in this thesis

In this thesis, organic or polymeric devices with thin layers are used to study transport in organic/polymeric materials under electric and optical fields. Field effect transistors are used for studies of the influences on polymeric thin layers under electric field, while photovoltaic cells are used to study optically driven transport in charge-harvesting dendritic materials.

In Chapter 2, electric and optical materials based on organics or polymers are introduced to describe electronic states. In Chapter 3, transport and charge transfer by optical process are explained briefly. Semiconducting polymers are made of conjugated polymers, which have repeated alternations of single-double bonds along carbon backbone chains. A microscopic description of conjugated polymer, so called, SSH model (Su-Schrieffer-Heeger) will be briefly introduced. Because most polymeric materials have disordered morphologies, some models about disorders on conjugated polymers are introduced. For optical materials, transport of excited charges after photon-absorption is important to understand photovoltaic cells. This includes energy transfer from one system to the other system.

Dendritic macromolecules are used for studies of optical charge transport in this thesis. These macromolecules have porphyrin derivatives because they have many absorption peaks in visible range. Electronic states in a porphyrin will be introduced in terms of quantum chemical molecular orbitals.

In Chapter 4, basic characterizations of electric and optical devices are introduced such as IV characteristic curves. In Chapter 5, fabrication of field effect transistors is explained briefly and their performances are presented. For these field effect transistors, Bayer’s Baytron P™, (poly(3,4ethylenedioxythiophene) doped by polystyrene
sulfonic acid), is used for active layers in the transistors. In Chapter 6, electric circuit elements such as amplifiers and current limiters are constructed.

In Chapter 7, charge transport studies of dendrons in photovoltaic cells are presented by both optical and electric characterizations. Steady-state photoluminescence spectra and fluorescence lifetime elucidate charge transfers within and between the dendritic molecules. In addition, electric characterizations of photovoltaic cells enable us to know incident wavelength dependence of charge transport in the dendrons.

In Chapter 8, transport in the electric and optical materials will be summarized and future prospects of this thesis will be presented.
2.1 Overview of conjugated polymers

Conducting polymers are made of conjugated polymers and chemical dopings on conjugated polymers create more charge carriers. A conjugated polymer is a carbon chained polymer with repeating single-double bonds, which are related to $sp^2$ hybridizations in carbon atoms. Each neutral carbon has four valence electrons in a 2s orbital and three 2p orbitals ($2p_x$, $2p_y$, and $2p_z$). The 2s orbital and two of 2p orbitals ($2p_x$ and $2p_y$) are hybridized to become $sp^2$ orbitals, which contribute three $\sigma$ bonds by sharing the $sp^2$ electrons with the neighboring atoms. The other orbital of $2p_z$ contributes a $\pi$ bond. $\sigma$ bond is a strong bond with the energy difference of approximately 10 eV between $\sigma$-bond and $\sigma^*$-antibond [14]. Thus, $\sigma$ bond is electrically insulating and it is not suitable for electric transport. $\pi$ electrons can make conjugated polymers conductive if they form electronic crystals with a smaller lattice constant than a critical length [15, 16]. But due to electron-phonon interactions and Peierls instabilities in conjugated polymers, pairs of $\pi$ electrons appear to open a band gap of approximately 2 eV. This energy gap is relatively high, compared with
that of silicon or germanium. Pristine conjugated polymers are not highly conductive unless they are doped by dopants such as acids and halides.

Polyacetylene is the simplest example of conjugated polymers and it is more conductive with chemical doping [1]. Two possible structures are present in polyacetylenes, "trans"-polyacetylene and "cis"-polyacetylene. Trans-polyacetylene has degenerated ground states, but cis-polyacetylene does not. These polyacetylene systems are close to 1 dimensional semiconductors with band gap energy of approximately 1.8 eV, which can be measured by reflectance spectra [13]. Except a few
conjugated polymers such as *trans*-polyacetylene, which is symmetric for interchange of single and double bonds, most conjugated polymers have non-degenerated ground states such as *cis*-polyacetylene and polythiophene.

### 2.2 Optical organic and polymer materials

Since the first organic light emitting diode with 8-hydroxyquinoline aluminum (Alq₃) (Figure 2.4) was introduced by Tang *et al.* [17], organic/polymeric materials have stimulated many researchers to study mechanisms of photonic processes inside of them and to develop new techniques and materials. Later, luminescence from conjugated polymers, poly(*p*-phenylene vinylene), was reported by Burroughes *et al.* [18]. In addition, the collection of photon energy at planar heterojunction of copper phthalocyanine and perylene tetracarboxyl derivative was demonstrated by Tang [19]. Due to stronger photonic properties than other small organic molecules
or conjugated semi-conducting polymers, these optical materials (Figure 2.4) provide great possibility to fabricate light emitting devices and photovoltaic devices [17].

However, fluorescence in optical materials is not always a good factor for photovoltaic devices due to fast recombination of hole-electron pairs (or short lifetime of excitons). Efficiencies to convert light energy to electric energy can be poor in efficient fluorescent materials. Some agents to separate these hole and electron pairs are required to overcome fast recombinations of the hole-electron pairs in photovoltaic cells. For an example, a strong electron accepter, fullerene (C\textsubscript{60}), helps charge separation by accepting photo-generated charges from optical polymers within an order of picosecond [20].

Another problem in organic/polymeric photovoltaic devices is that organic/polymer materials have short charge diffusion lengths, approximately 10 nm. Most of organic/polymeric materials rely on hopping conduction rather than band conduction. Thus, this causes another problems in photovoltaic devices, small light absorption

Figure 2.3: Absorption spectra of cis-polyacetylene (left) and trans-polyacetylene (right) (from Ref. [13]).
Figure 2.4: Organic and polymeric materials for light emitting and photovoltaic devices. 8-hydroxyquinoline aluminum (Alq₃ : left, from Ref. [17]), poly p-phenylene vinylene (Pp-PV : center, from Ref. [18]), and copper phthalocyanine (CuPc : right, from Ref. [19])

within charge-carrier diffusion length by photovoltaic material and difficulty in fabricating very thin layered devices of the diffusion length.

Interfaces between organic active layers and metallic electrodes are important in photovoltaic devices because interface barriers can block charge collection by electrodes. For hole collection by anodes, there are many hole-transporting materials, such as poly(ethylenedioxythiophene) / poly(styrenesulfonate) (PEDOT/PSS) and polyaniline. However, electron transporting materials are rare. Thus, there are many photovoltaic devices reported, which do not have electron-transporting layers. Recently, inorganic/organic hybrid solar cells are reported using metal oxides such as TiO₂, ZnO, SnO to accept photo-excited electrons [21, 22, 23, 24, 25]. These oxides have lowest unoccupied molecular orbital (LUMO) levels of approximately 4 eV below the vacuum level, and band gap energies are more than 3 eV [26]. Thus, these metal oxides can be good electron accepters due to better couplings to LUMO levels
of usual organic semiconductors, and they also serve as good hole-blocking layers to prevent hole-electron recombination.
CHAPTER 3

ELECTRIC AND OPTICAL PROPERTIES OF ORGANIC AND POLYMERIC MATERIALS

3.1 Conducting polymer model: electron-phonon interaction

One of popular models to describe transports in conjugated polymers uses tight binding model with electron-phonon interactions, so called, SSH model (Su-Schrieffer-Heeger) [27, 28, 29].

The Hamiltonian is written as

\[
H = \sum_{n,s} (t_{n,n+1}c_{n+1,s}^\dagger c_{n,s} + \text{h.c.}) + \sum_n \left( \frac{p_n^2}{2M} + \frac{1}{2}K(u_n + u_{n+1})^2 \right)
\]  

(3.1)

where \(c_{n,s}^\dagger, c_{n,s}\) are creation, annihilation operators at the \(n\)th CH site for \(s\) spin state, \(M\) is the effective mass of a CH group, \(K\) is a spring constant between adjacent CH groups, \(u_n\) is deviating distance from equilibrium site of the \(n\)th CH group, and \(t_{n,n+1}\) is the electronic transfer rate from site \(n\) to site \(n+1\), which is approximated as

\[
t_{n,n+1} = -t_0 + \alpha(u_n - u_{n+1})
\]

(3.2)

When a polyacetylene is stabilized, Peierls effects result in [32],

\[
u_n = (-1)^n u_0
\]

(3.3)
Thus, the Hamiltonian is expressed in the sum of terms about hopping of $\pi$-electrons across CC bond, electron-phonon coupling, and phonon’s kinetic/potential energies $(T + U)$.

$$
H = -t_0 \sum_{n,s} (c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s}) - 2\alpha \sum_{n,s} (-1)^n u_0 (c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s}) + (T + U)
$$

(3.4)

After doping of conjugated polymers, the signs of $u_n$ at doping sites do not alternate at the doping sites, i.e. there are discontinuities of the alternations. In Figure 3.1: A soliton on a trans-polyacetylene (top). A polaron and a bipolaron in a cis-polyacetylene(bottom).
Figure 3.2: Optical absorption spectra in *trans*-polyacetylene (top, from Ref. [30]) and polythiophene (bottom, from Ref. [31]). For the top plot, the doping rate (AsF$_5$) changes from zero (Curve 0) to the highest (Curve 5) except Curve 4, whose doping rate is compensated by NH$_3$. For the bottom plot, electrochemical doping rate with ClO$_4^-$ is changed by varying applying voltage.
3.1, electronic states of a soliton, a polaron, and a bipolaron are shown. Solitons are generally considered in degenerated conjugated polymers. After doping, an electron is added (negative soliton, $Q = -e, S = 0$) or removed (positive soliton, $Q = +e, S = 0$) [28]. After photo-excitation, a double bond is broken to leave a single electron (neutral soliton, $Q = 0, S = 1/2$) at a carbon atom [28]. These solitons are free to move by intra-molecular hoppings.

When more solitons appear in a polymer chain, it is possible to have bound states of two solitons. A polaron is a combined state of a charged soliton and a neutral soliton, which is a positive polaron ($Q = +e, S = 1/2$), or a negative polaron ($Q = -e, S = 1/2$) [28]. Thus, there is an energy split of two soliton levels in the middle of bandgap and one of the energy levels is half filled. Bipolarons are combined states of two charged polarons (positive bipolaron: $Q = +2e, S = 0$, negative bipolaron: $Q = -2e, S = 0$) [28].

Optical absorption spectra provide evidences of soliton [30], and polarons [31]. In the top plot in Figure 3.2, there is a small mid-gap absorption peak (about 0.9 eV), which is related to a soliton level [30]. In the bottom plot in Figure 3.2, two peaks appear approximately at 0.3 eV and 1.6 eV, which are polaron energy levels within the bandgap (about 2.2 eV) [31].

3.2 Conducting polymer model: disorder driven metal-insulator transition

In the previous section, the SSH model is very useful to explain charge transport of a single conjugated polymer. However, conducting polymers are usually formed as the collection of many polymer chains with random distributions. This limits application of the SSH model because it does not consider the nature of polymer structure.
On the contrast to delocalized Bloch waves in periodic conjugated polymers, impurities, sudden bends of polymers, and structural defects introduce localized states of charge carrier (Anderson localization) [35]. When there are many localized states by disorders, they form a band of localized states. As the degree of disorder is higher, the band of localized states is broadened [33]. This creates band tails that approach conduction and valence bands of semiconducting polymers to reduce the bandgap energies of the semiconducting polymers [36].

Actual polymer systems are not completely random. There are a number of small ordered regions of polymers [37]. The properties of these ordered regions depend on polymer preparation methods, such as choices of solvents (secondary doping) [38]. X-ray diffraction studies prove these ordered regions by showing resonant peaks [39]. Figure 3.4 shows a schematic diagram of islands of crystalline (ordered) polymers.
3.3 Transport at interfaces: charge injection

In transport measurements of a device, interfaces between two layers affect transport of the device. For examples, Schottky barriers can limit currents through devices at low applied electric fields. This section describes some transport phenomena, space charge limited current (SCLC) [40], Fowler-Nordheim law [41], and Poole-Frenkel effect [42, 43].

Before considering space charge limited current, it is good to consider an ideal case, charge conduction through an insulating layer. Consider a capacitor-typed device with capacitance per unit area of $C$, and thickness of $L$. Current density, $J$, is

$$J = \rho v = Q/t$$

(3.5)

, where $t$ is the time for charges to travel between two electrodes of the capacitor.
Capacitance per unit area, $C$, is

$$ C = \frac{\epsilon}{L} \quad (3.6) $$

Thus, charge per unit area, $Q$, is

$$ Q = CV = \frac{\epsilon V}{L} \quad (3.7) $$

The transit time, $t$ is

$$ t = \frac{L}{v} = \frac{L^2}{\mu V} \quad (3.8) $$

, where $\mu$ is the mobility of charge carriers.

Combining all of the above equations, we can get the relation between current density and the applied voltage between two electrodes.

$$ J = \epsilon \mu \frac{V^2}{L^3} \quad (3.9) $$

When the mobility of charge carriers is not high enough to drain out the charges inside of a capacitor-typed device, there exists net charge density (space charge) in the device. Poor charge transport at interfaces between electrodes and semiconducting media can also cause charge density in the device.

Poisson’s equation in 1 dimension is

$$ \frac{dE(x)}{dx} = \frac{\rho(x)}{\epsilon} = \frac{en(x)}{\epsilon} \quad (3.10) $$

where $E(x)$ is the electric field at the position, $x$. We assume that there is no local charge, such as trapped charge. $n$ is the number density of electrons.

Consider steady-state current density, $J$:

$$ J = n(x)e\mu E(x) \quad (3.11) $$
Multiplying $E(x)$ by $dE(x)/dx$, 

$$E(x)\frac{dE(x)}{dx} = \frac{1}{2} \frac{d(E(x)^2)}{dx} = \frac{J}{n(x)\epsilon\mu} \frac{en(x)}{\epsilon} = \frac{J}{\epsilon\mu}$$ \hspace{1cm} (3.12)$$

Integrating the above equation and assuming that there is no surface charge density at the interface (i.e. $E(x = 0) = 0$),

$$E(x) = \sqrt{\frac{2Jx}{\epsilon\mu}}$$ \hspace{1cm} (3.13)$$

With an additional assumption that there is no potential drop at both interfaces of the device,

$$V = \int_0^L E(x)dx = \sqrt{\frac{2J}{\epsilon\mu} \frac{2}{3} L^{3/2}}$$ \hspace{1cm} (3.14)$$

Thus, the current density is

$$J = \frac{9}{8} \epsilon\mu \frac{V^2}{L^3}$$ \hspace{1cm} (3.15)$$

An extra factor, $\frac{9}{8}$, is added in Eq. 3.15. Eq. 3.9 describes charge conduction without any accumulated charge in the transport medium while Eq. 3.15 describes the charge conduction with accumulated charge in the transport medium.

Fowler-Nordheim equation describes more realistic devices [41] by considering barriers at interfaces between electrodes and semiconductor media. For examples, thin oxide barriers generally exist between electrodes and semiconducting media. Fowler and Nordheim approximated a barrier as a triangular potential, shown in Figure 3.5. After quantum mechanical calculations, Fowler-Nordheim current is

$$J \propto E^2 \exp \left[ -\frac{2\sqrt{2qm^*u_B^2}}{3\hbar E} \right]$$ \hspace{1cm} (3.16)$$

Charge traps may appear in the vicinity of interfaces between charge-transporting media and electrodes. Poole-Frenkel law describes the charge injection into poorly
conductive semiconductors or insulators. It describes charge injection through lowered barriers by an external linear potential. The lowered potential enhances thermally assisted charge penetration at the interfaces. Poole described conductivity, $\sigma$, as

$$\sigma = \sigma_0 \exp(\beta E^\alpha) \quad (3.17)$$

Frenkel added a linear potential, provided by an externally applied voltage, into a Coulombic trap potential shown in Figure 3.6. At the interface, the potential energy around an electrode is described as

$$U(x) = -eEx - \frac{\kappa e^2}{\epsilon} x \quad (3.18)$$

, where $\kappa$ is a geometric factor. This will have a maximum point at $x_0 = \sqrt{\frac{e\kappa}{\epsilon E}}$.

The potential difference with and without the linear potential is

$$\Delta U(x_0) = \left(\frac{e^3\kappa}{\epsilon} E \right)^{1/2} \quad (3.19)$$

This difference is used to obtain the relation between conductivity and electric field.

$$\sigma \propto \exp(\Delta U/k_B T)$$

$$\sigma = \sigma_0 \exp \left[ \left(\frac{e^3\kappa}{\epsilon} E \right)^{1/2} / k_B T \right] \quad (3.20)$$
3.4 Energy transfer processes

Energy transfers between photons and electrons are considered in optical materials, for examples, photo-electron generation by light absorption and light emission after hole-electron recombination. Energy transport after photo-excitation is also important, especially in photovoltaic devices.

For photo-luminescence, radiative relaxation process, electronic energy is converted to photonic energy, and fluorescence and phosphorescence are examples of this process. Fluorescence is luminescence from recombination of singlet hole-electron pairs. This process is quantum-mechanically allowed to be fast within 1 nanosecond. Phosphorescence appears when the recombination of holes and excited electrons is
not quantum-mechanically allowed because hole-electron pairs are triplet. Extra interactions are required to recombine these triplet hole-electron pairs, which causes longer life times to be microseconds to second.

In light emitting devices, recombination of excited electrons and holes is the most important process. Statistically, only 25 percent of hole-electron pairs are ready to recombine to emit fluorescence and the other pairs cannot recombine to emit light. Thus, converting triplet pairs to singlet pairs is desirable in light emitting devices.

For photovoltaic cells, recombination of hole-electron pairs is not desirable so triplet pairs are more useful to preserve photo-generated charge carriers. However, just after photo-absorption in optical materials, singlet hole-electron pairs are generated. Without any transformation of these pairs, they will recombine quickly to lose their electronic energies. Thus, another processes for these photo-generated pairs
are required to separate electrons from the pairs. In addition, transport of separated charges should be considered. For an example, excited electrons are transferred to another systems via Förster processes and Dexter processes.

Förster process is the energy transfer via radiation or dipole-dipole interaction between a photo-excited system and an energy-receiving system [44]. The transfer rate, \( \Gamma \), in this process is proportional to the Coulombic interaction between dipoles of two systems. Because each dipolar interaction is proportional to \( 1/R^3 \),

\[
\Gamma \propto \kappa^2 J \left( \frac{R_0}{R} \right)^6
\]  

(3.21)

, where \( \kappa \) is the orientation factor between the two dipoles, \( J \) is the energy matching factor between the two systems, \( R \) is the distance between the two systems, and \( R_0 \) is a characteristic distance, typically, approximately 5 nm. In a Förster process, the spin of each system is conserved. Because this process is radiative, only energy transfers of singlet-singlet or triplet-triplet in the energy receiver are allowed.

\[
\begin{align*}
^1D^* + ^1A & \rightarrow ^1D + ^1A^* \\
^1D^* + ^3A_n & \rightarrow ^1D + ^3A_{m}^*
\end{align*}
\]  

(3.22)

When two systems are linked by a linker whose energy level overlaps to the two systems, an energy transfer through this linker is possible by exchanging electrons (Dexter energy transfer) [45]. The transfer rate is proportional to the extent to which energy levels are overlapped. If we assume that a wavefunction is simply exponential-decaying, \( \psi \propto e^{-R} \), the transfer rate, \( \Gamma \), is roughly written as

\[
\Gamma \propto J \exp(-R/R_0)
\]

(3.23)
where, $J$ is an overlapping integral between the two systems via the linker.

In Dexter processes, the total spin of the system is conserved.

$$^3D^* + ^1A \longrightarrow ^1D + ^3A^*$$  \hspace{1cm} (3.24)

The difference between the two energy transfer processes is the feasibility of different spin transfer. Förster process is also dependent on oscillator strength because radiative process is involved.

### 3.5 Electronic states in porphyrin

Porphyrin derivatives are popular materials for organic photovoltaic application due to many absorption peaks in visible wavelengths. Four pyrrole rings ($\text{C}_4\text{H}_4\text{NH}$)
(Figure 3.10) are connected with four methyl groups (CH) to create a porphyrin ring, a cyclic conjugated backbone system. Note that four nitrogen atoms are used to link four pyrrole rings in a phthalocyanine molecule. Absorption spectra of porphyrin and phthalocyanine are similar [46]. Strong absorption peaks are located in near blue wavelengths (approximately 420 nm), which are called the Soret band (B band). In addition, more peaks are observed in the wavelength from 500 nm to 700 nm (Q band). Figure 3.9 shows a Jablonski diagram for a typical porphyrin system [47].

The Soret band has a very strong absorption coefficient compared with Q bands. For a Zn-porphyrin system, the absorption coefficient for the Soret band is almost 100 times larger than those for Q bands [48]. This is due to constructive configuration interaction between two molecular orbitals to make up the Soret band, which will be described later.

Florescence from the Soret band is weak considering its strong absorption. Most of excited electrons to S2 levels are relaxed to S1 levels with very fast internal conversion (IC) so that the elapsed time in this process is ignored [49].

There are two fluorescence peaks, Q(0,0) and Q(0,1), thus vibration levels split the fluorescence peaks. Although these two fluorescence peaks are slightly stronger than fluorescence from Soret band, porphyrin is not an efficient fluorescent material. In addition, inter-system crossing to triplet states should be considered. However, there is little amount of reports about significant phosphorescence observation in porphyrin molecules. Usually, phosphorescence is very weak compared to fluorescence and its life time is on the order of 0.1 msec [50]. But introduction of a metal atom into a porphyrin ring enhances inter-system crossing to provide stronger phosphorescence.
For free based porphyrin, we have two-fold rotational symmetry. Thus, there are x-axis vibration and y-axis vibration of the ring. This symmetry provides additional Q bands in the absorption spectrum to provide four Q bands ($2 \times 2 = 4$). However, a metal based porphyrin usually has four-fold rotational symmetry to eliminate difference between x-axis vibration and y-axis vibration. Thus, two absorption peaks for Q bands are typically observed.

To understand the electronic structure of a porphyrin ring, first, consider the electronic structure of a pyrrole ring. A pyrrole ring has five atoms in an aromatic
ring, but it has six $\pi$ electrons due to a lone pair in the nitrogen atom. Assuming that the nitrogen atom in a pyrrole ring has the same properties as a carbon atom, the energy level for $\pi$ electrons has a pentagonal shape, shown in Figure 3.10 [51, 52].

Highest occupied molecular orbital (HOMO) of a pyrrole ring has the symmetry of $e_y$, and this symmetry has high electronic density at two linking carbon atoms (two carbons neighboring the nitrogen atom) to provide good electronic transfer.

Four linkage groups (-CH=, methyl) are introduced to build a porphyrin system. There are also interactions between pyrroles and methyl linkage groups, shown in Figure 3.11. Molecular orbitals of $e_y$ in four porphyrin rings well interact with those
Figure 3.11: Molecular orbital interaction between four pyroles and four linking -CH= groups. Hashed lines are Goutermans four orbitals (1a\textsubscript{1u}, 4a\textsubscript{2u}, 5e\textsubscript{g,xx}, 5e\textsubscript{g,yz}) (from Ref. [51]).

in methyl linkages, and large splits of energy levels appear in this combined system. Some of the new molecular orbitals, 5e\textsubscript{g,xx}, 5e\textsubscript{g,yz}, provide new lowest unoccupied molecular orbitals (LUMO), which will play roles to provide Soret and Q band absorption peaks. When we have four-fold symmetry in the porphyrin ring, these two e-symmetry molecular orbitals are degenerated to provide only two Q band absorption peaks. A free based porphyrin provides four absorption peaks due to destroyed symmetry in 5e\textsubscript{g,xx}, 5e\textsubscript{g,yz} molecular orbitals.
$e_z$ symmetry molecular orbitals in the four pyrroles do not interact with the molecular orbitals in methyl linkages due to different symmetry. These energy levels are almost unchanged and $1a_{1u}$ and $4a_{2u}$ provide HOMO levels for a porphyrin ring.

These four molecular orbitals, $1a_{1u}$, $4a_{2u}$, $5e_{g,xz}$, and $5e_{g,yz}$, were considered by Gouterman [46]. According to quantum chemical computation, the two HOMO levels ($1a_{1u}$, $4a_{2u}$) are not spaced by more than 1 eV (energy difference of Soret and Q bands), but very close to each other. A simple theory about molecular orbitals cannot account for large energy difference of Soret and Q bands. Configuration interaction is now considered, as a result, mixing of two exciting processes, configuration $(1a_{1u}, 5e_g)$ and configuration $(4a_{2u}, 5e_g)$, can answer the difference of the absorption energies and their absorption coefficients.

To formulate this, Hamiltonian for an absorption process from state $a$ to $b$ is expressed as

$$H_{eff}(ab) = E(ab)$$ (3.25)

where $H_{eff}$ is an effective Hamiltonian for absorption process. Between two configurations, there are additional terms for the interaction between configurations. Thus, total Hamiltonian is written as

$$H = H_{eff} + H'$$ (3.26)

$H'$ is mostly from Coulomb interactions and when two configurations have a similar symmetry, configuration mixing is considerable [53]. According to the results of quantum chemistry computation, the mixing ratio is almost 50:50, and we can approximate absorptions in Soret (B band) and Q bands as

$$|B> = \frac{1}{\sqrt{2}}((1a_{1u}, 5e_g) + (4a_{2u}, 5e_g))$$ (3.27)
\[ |Q\rangle = \frac{1}{\sqrt{2}}((1a_{1u}, 5e_g) - (4a_{2u}, 5e_g)) \quad (3.28) \]

Due to the antisymmetric state in \( |Q\rangle \), absorbing probability is small and the symmetric state of \( |B\rangle \) provides large absorption.

Recently, there have been direct measurements of porphyrin derivatives by scanning tunneling microscopes (STM) to figure their electronic states [54, 55]. In these works, there is direct electron injection on LUMO states of porphyrin derivatives to observe luminescence.

In Figure 3.12, not all configurations of a zinc-ethioporphyrin molecule provide luminescence. Configurations with an extra lower energy peak show luminescence. The bias voltage on the probe tip with respect to substrate (NiAl/Al\(_2\)O\(_3\)) is 2.35 V and voltages at lower peaks in configuration A and B are approximately 0.8 V. From the luminescence plots in Figure 3.12, this is located at 1.5 eV. Thus, 2.35 V probe tip excitation on the zinc-ethioporphyrin molecule is identical with 3 eV optical excitation, which indicates that LUMO levels are related to the Soret band.

In Figure 3.13, similar luminescent plots are provided. Due to interaction between the substrate and the monolayer, samples with single and double layers do not provide characteristic luminescent features of porphyrin molecules whereas a sample with six monolayers shows characteristic luminescence spectrum of porphyrin molecules. Plot (c) in Figure 3.13 indicates dipole-dipole interactions, which remind us of Förster energy transfers.
Figure 3.12: STM images (top right) of zinc-ethioporphyrin (top left) with different states at 2.35V bias voltage and 0.1 nA current. In these plots, configurations A and B are luminescent and configurations C to F aren’t. Lower plots show luminescent from configuration A ($V_{bias} = 2.35V$, $I = 0.5$ nA) and B ($V_{bias} = 2.2V$, $I = 0.5$ nA) when the STM probe tip is located lobes 1 to 4 of porphyrin (from Ref. [54]).
Figure 3.13: STML (scanning tunneling microscope luminescence) of a porphyrin derivative at different molecule layers. For small-numbered monolayers, plasmons from the substrate affect to shade fluorescence of porphyrin molecules. Plot (c) shows linewidth of fluorescence at 658nm from the samples with 3 to 6 monolayers (from Ref. [55]).
4.1 Organic field effect transistor

The first transistor based on inorganic semiconductor was invented by Bardeen, Brattain, and Shockley from germanium in 1947 [56]. Before the invention of the bipolar transistor, the concept of field effect transistors was already patented [57] in the early 1930’s and after further studies in inorganic semiconductors in 1950’s, field effect transistors were developed in 1960’s [58]. These inorganic materials such as germanium, silicon, and compound of gallium and arsenide, have been a major part of modern electronics in parallel with developments in material purification and micro-fabrication.

Organic materials based on carbon atoms were not used for field effect transistors until in the middle 1980’s. Discoveries of semiconducting and conducting organic materials, and the development of inorganic transistors gave motivations to develop organic transistors.

An Electrochemical transistor is one of early organic transistors. The Wrighton group has reported micro-electrochemical field effect transistors using polypyrrole[59],
Figure 4.1: Electrochemical field effect transistors with poly(3-methylthiophene) in reversible redox process (top), IV curves (bottom left), and saturation effects (bottom right) (from Ref. [60]).

poly(3-methylthiophene)[60], and polyaniline [61]. These transistors use reversible reduction-oxidation processes of the above conducting polymers under electrolytes such as CH₃CN and LiClO₄ aquatic solutions. Although these transistors make uses of the redox processes, there are some features such as the existence of saturated drain-source currents, which also appear in conventional Si based field effect transistors.

Field effect transistors without chemical redox process were fabricated with copper phthalocyanine [62], undoped polythiophene [63, 64], α-hexylthiophene [65], polyacetylene [66, 67], and pentacene [68]. It is possible to fabricate all-organic transistors [69]. Materials used for field effect transistors are categorized into small semiconductor molecules and semiconducting polymers.
Transistors with small molecules have relatively good quality of materials and have characteristics that are very dependent on crystallinity of the materials. Early transistors were mostly p-typed transistors because most small molecules are hole transporting materials. Recently, n-typed materials and high dielectric constant insulators have been developed to improve organic field effect transistors [70].

In contrast to organic/polymer semiconductors, field effect transistors based on “conductive” polymers were also realized by using poly(3,4-ethylenedioxythiophene) doped with polystyrenesulfonic acid (PEDOT/PSS) [34, 39, 71, 72, 73, 74]. These transistors are not redox processed transistors, supported by visible and Fourier-transformed-infrared (FTIR) spectrum studies of PEDOT/PSS channel layers of transistors [75], and investigation of charge carrier population inside transistor channels by electron paramagnetic resonance (EPR) [76].
4.2 Field effect transistor models

A field effect transistor consists of a gate electrode, an insulating layer, an active layer, and contact electrodes for the active layer. An electric field from the gate electrode is transmitted through the insulating layer and modifies the transport properties of the active layer. The structure of gate/insulating layer/active layer is a capacitor structure. Charges in the active layer can be accumulated or depleted by applying gate voltage.

For conventional silicon based and well-crystalline organic field effect transistors, charges accumulated in the active layers of the transistors are close to free charges depending upon the band structures of the active layers [3, 77]. However, for some organic and polymer transistors, transport of hopping conduction is considered due to disorders in the materials. Hopping transport can be controlled by gate electric field, which will be introduced in the following section briefly.

With an assumption of slow field variance along an active channel layer (Figure 4.2),

\[ \frac{\partial E}{\partial z} \gg \frac{\partial E}{\partial x} \]  

(4.1)

Poisson’s equation for charge density in active layer is constructed as

\[ \frac{\partial^2 V}{\partial z^2} = -\frac{\rho}{\epsilon_s} \]  

(4.2)

Assume that the charge density is constant at a certain vertical extension (\( \rho = \rho_0 \) in \( 0 < z < W \)), integrating the above equation twice gives

\[ V(z) = V_s(x) - \frac{\rho_0}{2\epsilon_s} (z - W)^2 + \frac{\rho_0}{2\epsilon_s} W^2 \]  

(4.3)

where \( V_s(x) \) is the potential at the boundary between the active layer and the insulating layer.
Without applying any drain-source voltage, potential is zero at \( z = W \) (i.e. grounded),

\[
W = \sqrt{-2\epsilon_s V_s(x)/\rho_0}
\]  

(4.4)

where \( W \) is the depth of the charge carrier channel, which decides the trans-conductivity between source and drain electrodes. Gate voltage can affect the boundary potential, \( V_s \), which can create the charge carrier channel beneath oxide layer. Charge density, \( \rho_0 \), is related to doping rate.

When drain and source voltages are low, the channel depth is uniform across the channel, and the drain-source current is

\[
I_{DS} = \frac{W C_{OX} \mu}{L} (V_{GS} - V_T - V_{DS}/2)V_{DS}
\]  

(4.5)

where \( W \) is the width of the channel, \( L \) is the length of the channel, \( V_T \) is a threshold voltage which depends on gate electrode materials, \( \mu \) is the mobility of induced charge carriers, and \( C_{OX} \) is the capacitance of the insulating layer per unit area. Ignoring last term of the above equation, there is a linear relationship between \( I_{DS} \) and \( V_{DS} \).

Although the surface potential on the active layer varies slowly along the channel, surface potentials near the source and the drain are sufficiently different to cause different channel depths when the drain-source voltage is high. We expect bottle-neck effects across the channel. In this case, the channel depth at the bottle-neck discourages transconduction, but the strong electric field from drain-source voltage encourages it. Therefore saturation effects in drain-source currents appear.

\[
I_{DS, sat} = \frac{W C \mu}{2L} (V_{GS} - V_T)^2
\]  

(4.6)
Figure 4.3: Ions interact with hopping sites in disordered region of polymers. Thus, only long-range hopping is possible so that poor charge transport appears in this figure (from Ref. [39]).

To measure field effect mobility of charge carriers, there are two methods, which utilize either the linear region or saturated region of a field effect transistor’s IV characteristic curves.

4.3 Controlled hopping model

Charge transport in conducting polymers is between islands of well-ordered polymers. Between these islands, localized quantum states exists, providing charge hopping. However, in amorphous (disordered) areas, ions are relatively free to move. These ions can affect charge-hopping quantum states. Thus, the hopping distance is longer if states are not available by ions. Hsu et al. utilized ions embedded in a polymeric insulating layer of a field effect transistor [39, 74]. Gate voltage can push or pull ions into the active channels of transistors to block hopping sites as shown in Figure 4.3.
4.4 General characterization of photovoltaic devices

Photovoltaic devices collect light energy and convert it to electrical energy. Suppose that there is semiconducting material with an energy gap. When a photon with higher energy than the bandgap hits the material, a hole-electron pair (an exciton) is generated. This system is excited by at least the bandgap of the material. And the light energy is transmitted to an energetic electron in the system.

It is highly possible that this hole-electron pair will recombine to produce another photon. Therefore, we need to separate this pair before recombination. One method to separate this hole-electron pair is to use an internal electric field which is provided by a hetero-junction between the electron donors and accepters.

This structure provides high efficiency at the hetero-junction point. However, photogenerated charge away from the point is not affected by the internal electric field, reducing the efficiency of photovoltaic devices. The solution to this problem is to extend the hetero-junction area, making zigzag cross-sectional features in the junction [78]. This fabrication is difficult and it is not appropriate for low cost devices.
However, for organic and polymer materials, it is possible to have solution processes and we can control the properties of the solutions. When two unmixable solutions are blended and sandwiched (Figure 4.5), the hetero-junction area increases due to the three-dimensional mixing structures [79].

If there is no incident light on photovoltaic device, it is just a Schottky diode, and follows the diode equation

\[ I = I_0(\exp(\eta V/k_B T) - 1) \]  (4.7)

With incident light, the photocurrent generated in the device is

\[ I = I_0(\exp(\eta V/k_B T) - 1) - I_{SC} \]  (4.8)

Short circuit current (\(I_{SC}\)) is the current when cathode and anode are connected to each other and purely from the photogenerated current. Open circuit voltage (\(V_{OC}\)) is the voltage when cathode and anode are disconnected, dependent on the choices of anode and cathode material work functions. Filled factor (FF) is a ratio of the maximum value of voltage-current product to product of \(I_{SC}\) and \(V_{OC}\), shown in Figure 4.6. Filled factor of 1 is ideal for photovoltaic cells, but it does not always
Figure 4.6: A schematic IV curve of a photovoltaic device.

indicate high efficiency in photovoltaic devices. We also need to consider the open circuit voltage and the short circuit current.
CHAPTER 5

FABRICATION OF THIN FILM POLYMER TRANSISTORS

5.1 Transistor fabrication procedure

Thin film polymer transistors have the structure: active channel layer, insulating layer, gate electrode layer, and source and drain electrodes. Active layers are created from dispersive solution of poly(3,4-ethylenedioxy thiophene) (PEDOT) doped by polystyrenesulfonic acid (PSS) (Baytron P™ from Bayer) [80]. PEDOT is an oligomer with several monomers doped by long PSS [81]. This solution provides heat resistant films, which can endure up to 200 °C. However, this solution does not produce good conductive thin films ($\sigma \sim 10^{-3}$ S/cm). Dispersion solution requires filtration in a 5 µm syringe filter. We mix 80% filtered Baytron P™ and 20% ethylene glycol (ethan-1,2-diol, $C_2H_4(OH)_2$) by volume to enhance conductivity of films (secondary doping [38]). These films generally have conductivity of 25 S/cm. To enhance adhesion of the films on glass substrates, we add one droplet (approximately 0.02 ml) of dodecylbenzene sulfonic acid (DBSA, $C_{12}H_{25}C_6H_4SO_3H$, Acros Organics) in 10 ml of mixed solution, which has both hydrophilic and hydrophobic functional groups.
Slide glass is used for substrate and is cleaned with acetone and methyl alcohol to remove grease and other contamination. Then, we make a pattern for the active channel layer by applying normal office tape. Prepared Baytron P™ solution is spin-coated on the substrate at 2000 rpm to generate an active film of approximately 100 nm thickness. After removal of the tape pattern, we dry the film by baking it on a hot plate at 200 °C for one minute or leave it under ambient conditions for one day.

After drying the Baytron P™ film, the source and drain electrodes are deposited by thermal evaporation of silver, which is stable in air. Then, an insulating layer of polyvinylphenol is added by spin-coating using poly(4-vinylphenol) (Sigma-Aldrich, m.w. ~ 20,000) solution, prepared by dissolving it in isopropanol with approximately 1% concentration by weight. This solution is spin-coated at 2000 rpm and annealed for 30 minute at 200 °C under low vacuum because the glass temperature of poly(4-vinylphenol) ranges from 130 to 185 °C. Very thin insulating layers are used to improve device performance [82]. But for ultra-thin insulating films, no annealing process is carried out.

Finally, a gate electrode is deposited by careful thermal evaporation of aluminum under the pressure of mid to low 10^{-6} torr to prevent the oxidation of aluminum during evaporation. The evaporation rate is less than 2 Å/sec and the thickness of aluminum is approximately 300 Å not to damage the insulating layer and the active channel layer.

5.2 Device characteristics

To observe the performance of field effect devices, two kinds of device characterization are carried out. One is to obtain transient drain current responses under gate
voltages and the other is to obtain IV characteristic curves. Since the dielectric layer
thickness is minimized, relatively fast response under low gate voltage is achieved.

Figure 5.3 shows transient responses of a polymer field effect transistor (Baytron
P/Polyvinylphenol/Aluminum). In this plot, we observe a p-type transistor due to
poorer conductivity at higher gate-source voltage. In this transistor, the insulating
polyvinylphenol layer is approximately 20 nm thick and the aluminum gate layer
is also approximately 20 nm thick. The falling response time of the drain-source
current is less than 0.5 second, which is an interval time of data acquisition. The
response time of the drain-source current in the absence of gate electric field is very
long on the order of 10 seconds to of 100 seconds. This shows that the triggering
sources controlling conductivity of the transistor’s channel are very sensitive to the
gate electric field, but not too mobile to diffuse into the channel material media. The
plausible sources of triggering ON/OFF states in the field effect transistor, are ions,
as they are much heavier than electrons or holes.

The ON/OFF ratio of the transistor in Figure 5.3 is approximately $10^3$. In other
work, this has been shown to reach $10^6$ [76]. Even a small gate-source voltage about
0.5 V enables the device to control channel conductivity, that is an advantage of thin
insulating layer.

In Figure 5.4, the explanation of ion involvement is clearer. At time of about 27
second with gate-source voltage of -3V, the recovery of drain-source current is much
faster than for zero gate-source voltage.

Figure 5.5 shows IV the characteristics of a polymer field effect transistor. This
plot also shows a p-typed transistor because saturated drain-source currents are ob-
erved at a negative drain-source voltage. According to the conventional field effect
transistor theory, field effect mobility of positive charge carriers is [77]

\[ I_{\text{sat}} = \frac{WC}{2L} \mu (V_{gs} - V_{\text{th}})^2 \]  \hspace{1cm} (5.1)

where \( I_{\text{sat}} \) is the saturation current, \( W \) is the width of the channel, \( L \) is the width of the gate corresponding to the length of the channel, \( C \) is the capacitance per unit area of the insulating layer, \( \mu \) is the field effect mobility, \( V_{gs} \) is the gate-source voltage, and \( V_{\text{th}} \) is the threshold voltage.

Applying the above equation, we obtain a field effect mobility of 10 \( \text{cm}^2/V \cdot \text{sec} \), which is relatively high in semiconducting organic/polymer materials. Even well prepared crystalline pentacene is reported to have a mobility of approximately 10 \( \text{cm}^2/V \cdot \text{sec} \) [83]. Thus, a different process is involved in this polymer field effect transistor. Note that the above equation holds for any switching device, which has the effect of pinching free charge carriers along the conductive channel by external factors. However, our field effect devices make use of electric field to control heavy ions, which are not actual charge carriers in the channel. Thus, there is a contradiction, slow mobility of ions, and the sensitive effect of the ions under an electric field from gate electrode. This contradiction indicates that ions block hopping sites of charge carriers in the active layer of the transistor under the gate electric field. Without the gate electric field, these ions are released from the hopping sites to recover the conductivity of the active layer.
Figure 5.1: Poly(ethylenedioxythiophene) (top) and Poly(styrenesulfonate) (center) compose Baytron P™ used for channel active layers. Poly(4-vinylphenol) is used for insulating layers (bottom).
Figure 5.2: Structure of a polymer thin film field effect transistor (top) and an optical micrograph of a transistor (bottom).
Figure 5.3: Transient responses of drain-source and gate-source currents in polymer field effect transistors (Baytron P / Polyvinylphenol / Aluminum) under gate-source voltage variation. Bottom plot uses the absolute value of the gate-source current on a logarithmic scale. Drain-source voltage is 1.4 V.
Figure 5.4: Transient responses of drain-source and gate-source currents in polymer field effect transistors (Baytron P/Polyvinylphenol/Aluminum) under larger gate voltage variation. Bottom plot shows detailed features for small currents.
Figure 5.5: IV characteristics of a polymer field effect transistor (Baytron P / Polyvinylphenol / Aluminum).
CHAPTER 6

APPLICATION OF THIN FILM POLYMER TRANSISTORS

This chapter provides applications of polymer transistors. Although the response time is on the order of 1 to 100 seconds, there are some methods to improve response times, which are illustrated in Section 6.3.

The fundamental functions of a field effect transistor are switching and amplifying signals. Switching signals have already been shown in Section 5.2 (transient responses of polymer field effect transistors under various gate-source voltages). Slow responding transistors are still useful for applications, for examples, active matrix displays [84, 85], which consist of switching transistors (or amplifying transistors) and organic light emitting cells, which require approximate 30 Hz refreshing frequency. Fast organic field effect transistors can be demonstrated by constructing a ring oscillator from an odd number of inverting amplifiers [86].

6.1 Application for inverting amplifiers

An inverting amplifier in this application consists of a field effect transistor and a resistor with a suitable resistance value. This resistance value determines amplification factor as well as the bandwidth of the amplification frequency. Figure 6.1 shows
the configuration of an inverting amplifier and its resultant signals. Input signals are sent to the gate electrode of the field effect transistor and output signals are seen at one end of the resistor.

Gate voltage (input signal) controls the transconductivity of the active channel in the transistor, which controls the drain-source current. Because voltage difference along the resistor depends only on the current through the resistor, which is the same as the drain-source current, we have an output voltage signal which is driven by the gate voltage.

With frequency of 0.025 Hz, output signal is closer to a square wave than when frequency is faster at 0.11 Hz. This distortion of output signal at the higher frequency indicates slow response of polymer field effect transistors. The cut-off frequency, at which amplification factor is one, is higher than 0.11 Hz.

6.2 Current source

A current source is a circuit configuration used to limit a current at a certain level regardless of the supply voltage. This, in principle, uses the saturation effect of a field effect transistor, which is shown in section 5.2. Figure 6.2 shows a circuit diagram for a current source that has only a field effect transistor with the drain and gate connected. For p-type field effect transistors, as drain voltage increases, the electric field between the source and gate becomes larger and blocks charge flow, but due to higher drain-source voltage, current flow does not change to observe a plateau region in a plot of drain-source current vs. drain-source voltage (Figure 6.2). Thus, a load will see infinite output impedance and the current is always constant regardless of load resistors.
Figure 6.1: Electric circuit diagram of inverting an amplifier using a 10 MΩ resistor and a polymer field effect transistor (left). Amplified signals of square waves with two different frequencies (right).
Figure 6.2: Electric circuit diagram of a current source (top) and a plot of current vs. drain-source voltage (bottom).
6.3 Prospects for polymer transistors

So far, two application circuits have been introduced in this chapter. There will be continuously development of electronic devices, especially for the incorporation with organic light emitting devices. In addition, polymer field effect transistors are intensively studied for other purposes, sensors to detect gas, pressure, and biological substances [87].

For performance improvement, there are several factors to work on for field effect transistors. Thin insulating layers or insulating layers with high dielectric constants increase the capacitance of transistors to make it easier to accumulate or deplete charge carriers [70]. Another factor is to make narrow channel transistors. For a given charge carrier mobility, a short channel length gives a short carrier traveling time from source to drain electrodes. One possible way to make a narrow gap is using the electro-migration of an electrode (Figure 6.3) [88]. Vertical channel field effect transistors also provide short channel lengths [89, 90, 91], which do not require high-resolved lithography methods to create short channels.
Figure 6.3: Optical micrographs of the electro-migration process to make a narrow gap. A silver electrode is used in this process.
CHAPTER 7

PHOTOVOLTAIC DEVICES WITH DENDRIMER SYSTEMS

This chapter will describe photovoltaic devices made with dendrimers of porphyrin derivatives and naphthalene derivatives. Porphyrin derivatives act as electron donors and naphthalene derivatives act as electron accepters. Thus, the dendrimers have two kinds of functional groups for more efficient charge separation and harvest.

First, sample dendrimers and their functions are explained briefly. Absorption spectra are measured to see their electronic states. Measurements of photoluminescences and fluorescence lifetimes are carried out to figure out the natures of charge transfer in the dendrimers.

Simple photovoltaic devices are fabricated and characterized electrically. Careful measurements of IV characteristic spectra are carried out to show details of charge transfer. Based on the optical and electric characterizations, a model of charge transfer in the dendrimer systems is proposed.

7.1 Photovoltaic devices based on dendritic materials

A dendrimer is a kind of chemical structures, which has a branch structure on each chemical link [92]. The term originates from "Dendron", a Greek word meaning
a tree [93]. Due to its structure, dendritic materials are useful to focus excited charges from its ends of branches to its core.

Dye molecules are usually employed as functional groups to absorb or to emit photons. One important issue is the charge transfer from the ends to the core. Employing two different kinds of dyes (one on the core and the others are at the ends of branches), one can check charge transfer by observing the fluorescence of the core dye [94].

In photovoltaic devices, donor/accepter system is generally used to separate photoexcited hole-electron pairs. Especially, for dendrimers, many electron-donors are located at the ends of branches and photoexcited electrons generated at the donors are driven to accepters to maximize collection of photo-energy. For electron-accepting groups, strong electron accepters, such as \( \text{C}_6\text{O} \), are widely used to collect photo-excited electrons from the donors [95].

7.2 Materials and absorption spectra

Absorption spectra provide electronic states in optical materials. In this section, absorption spectra of a donor (tetraphenylporphyrin), an accepter (derivative of naphthalenediimide), and three different dendrons are presented. Three different dendrons synthesized from tetraphenylporphyrin (donor) and naphthalenediimide (accepter) are used in this work [96]. These dendrons are first generation (G1) dendrons with two donors and one accepter. The chemical structures of the donor, the accepter, and the three different dendrons are shown in Figures 7.1 and 7.2.

A modification is made on Dendron B by substituting a Zinc atom with two hydrogen atoms in each porphyrin ring of Dendron A. Thus, the porphyrin ring with
Figure 7.1: Chemical structures of tetraphenylporphyrin (top left), naphthalenediimide (top right), and Dendron A (bottom). Courtesy of Yingqi Wu.
Figure 7.2: Chemical structures of modified dendrons, Dendron B and Dendron C. Courtesy of Yingqi Wu.
Figure 7.3: Ground states of Dendron A (top) and Dendron C (bottom) calculated by the Monte Carlo method (AMBER). Courtesy of Yingqi Wu.
a Zinc atom now has 4-fold symmetry and there are only two Q-Band absorption peaks. Dendron C has an extra ortho-phenyl linkage. This ortho-phenyl linkage has a relatively good transferring functional group similar to a para-phenyl linkage. However, this extra linkage reduces the rate of charge transport through the linkage, compared with Dendron A, and also causes a folded structure according to quantum chemical computation [96] shown in Figure 7.3.

In Figure 7.4, the absorption spectrum of the donor shows a clear Soret peak and four Q band peaks, which is typical for all other porphyrin derivatives. Acceptor absorption spectrum appears broad near UV band, which is not intensively overlapped with absorption peaks in the donor. This enables us to sensitize only one functional group of them, either tetraphenylporphyrin or naphthalenediimide derivative. We are interested in sensitizing tetraphenylporphyrin (donor) due to the many absorption peaks in the visible spectral range.

Two solvents for the donor, the accepter, and the Dendron A are used for absorption spectrum measurements, dichloromethane (CH$_2$Cl$_2$) and acetonitrile (CH$_3$CN). Acetonitril provides stronger polarity than dichloromethane due to the strong electron affinity of the cyanide functional group. In the solution of Dendron A in dichloromethane, absorption peaks from the accepter functional group and the Q bands are still present. However, in the solution of Dendron A in acetonitrile, those absorption peaks are much discouraged although the Soret band peak is still noticeable.

It will be shown that the Q bands in tetraphenylporphyrin (donor) couple better to near UV bands (around 370 nm) in naphthalenediimide than the Soret bands.
Figure 7.4: Absorption spectra of the donor (tetraphenylporphyrin), the accepter (derivative of naphthalenediimide), and the Dendron A in solution states. Courtesy of Yingqi Wu.
Figure 7.5: Absorption spectra of the donor (tetraphenylporphyrin), the accepter (derivative of naphthalenediimide), and three dendrons in solid film states.
do. Intra-molecular charge transfers take places from the donors to the accepters in Q-band illumination.

In the solid states of the donor, the accepter, and the dendrons, there are small peak shifts in the absorption spectra due to the stronger interactions between molecules or functional groups. In Figure 7.5, the absorption peaks from the donor become broader and similar features can be seen in all dendron films. Due to symmetry, two Q bands disappear in the absorption spectra of Dendron B film. From the absorption spectra of the dendrons, the interactions between the donor and the accepter in dendrons are weak because they are almost the sum of the absorption spectra of the donor and the accepter.

7.3 Steady-state photoluminescence measurement

Porphyrin and its derivatives have weak characteristic photoluminescence from red to near infrared color, which is close to the energy levels of the first excited singlet state. In this section, photoluminescence measurements are carried out and compared for samples of the donor (tetraphenylporphyrin), the accepter (naphthalenediimide), and the three dendrons in both solid and solution.

Figure 7.6 is a schematic diagram for the photoluminescence measurement. Photon Technology International’s (PTI) Quanta Master Series 1 (QM1) is used. Because the luminescence of the donor is very weak, we open slits widely on both monochromators to have a spectral resolution of 5 nm FWHM (full width at half maximum). A seventy five Watt Xenon lamp is used as an excitation light source and a photomultiplier tube (Hamamatsu’s R928) is used for a photon counting detector to cover near UV to near infrared spectral range. The scanning range of the excitation wavelength
Figure 7.6: Setup diagram of Photon Technology International’s Quanta Master 1 for photoluminescence measurement.
is from 300 nm to 765 nm in steps of 5 nm. The emission of photoluminescence is measured with a range from 20 nm higher than the emission wavelength to 800 nm. Multiples of excitation wavelengths are avoided in emission wavelength to protect the photon detector, because emission at multiples of excitation wavelength is extremely large due to optical interference effects.

Figure 7.7 shows the photoluminescence spectra for tetraphenylporphyrin (donor) and naphthalenediimide derivative (accepter) in solid film states. These films are actually parts of photovoltaic cells, which will be used in the later section. Photovoltaic cells have the structures of ITO/Al4083(hole transport layer)/donor or accepter/Aluminum. It is notable that the hole transport layer does not affect the photoluminescence spectra, which is confirmed by comparing the spectra with the photoluminescence spectra of the samples on bare glass substrates.

We observe photoluminescence in tetraphenylporphyrin at 660 nm and 730 nm. Although there is a dependence of solvent (tetrahydrofuran (THF: C₄H₈O) and chloroform (CHCl₃)) in photoluminescence, these data are typical for other kinds of porphyrin derivatives. A possible reason of solvent dependence is different crystal structures of resultant films. For naphthalenediimide derivatives, there is weak luminescence around 460 nm.

Figure 7.8 shows quenching of photoluminescence from the porphyrin group when formed as a dendritic macromolecule. All dendrons do not show characteristic luminescence peaks at 660 nm and 730 nm. Thus, the presence of the accepter functional groups eliminates the luminescence, which implies that charges are transferred from the donor functional groups to the accepter functional groups. Still, we cannot decide
Figure 7.7: Photoluminescence of tetraphenylporphyrin (left two) and naphthalenediimide (right two) from photovoltaic cells. Top two are films prepared from tetrahydrofuran (C₄H₈O) solution and bottom two are films from chloroform (CHCl₃) solution. Note that logarithm scales are used.
Figure 7.8: Photoluminescence of Dendron A (top left), Dendron B (top right), and Dendron C (bottom left) films from photovoltaic cells. Note that logarithm scales are used.
Figure 7.9: Photoluminescence of tetraphenylporphyrin (top) and naphthalenediimide (bottom) films on p-type Si wafers. The solvent used to prepare samples is chloroform (CHCl₃). The left two plots are drawn in linear scales and the right two plots are in logarithm scales.
Figure 7.10: Photoluminescence of tetraphenylporphyrin (top) and naphthalenediimide (bottom) films on p-type Si wafers. The solvent used to prepare samples is tetrahydrofuran (THF: C₄H₈O). The left two plots are drawn in linear scales and the right two plots are in logarithm scales.
Figure 7.11: Photoluminescence of Dendron A dissolved in chloroform (CHCl$_3$) (top two) and Dendron C dissolved in tetrahydrofuran (THF: C$_4$H$_8$O) (bottom two). Linear scale is used for left two plots and logarithm scale is used for right two plots.
what kind of charge transfer is carried out (intra-molecular or inter-molecular) at this moment.

In order to remove background luminescence from substrates, p-typed silicon wafers with resistivity of approximately 5 Ohm-cm are used as substrates. Figure 7.9 again shows luminescence of the donor and the accepter dissolved in chloroform. From the donor, we can see weak luminescence at 430 nm, which corresponds to Soret band. Thus, Soret band, $S_2$, is not a strong luminescent level compared with the lowest level of Q bands, $S_1$. From the accepter, we also see weak luminescence with central peak at 450 nm, and we can observe weaker luminescence from 500 nm to 600 nm.

Figure 7.11 clearly shows the difference of Dendron A and Dendron C. Dendron C has weak, discrete luminescence peaks, which corresponds to some of high energy Q bands. However, the emission peaks do not exactly match the absorption peaks of Dendron C. For the donor only sample, there is also similar luminescence, but weaker than that from Dendron C. For Dendron A, it is hard to observe high energy Q band luminescence. Thus, this implies more similarity of Dendron C to the donor rather than Dendron A to the donor.

In contrast to the solid samples of dendrons, all solution samples of the dendrons show luminescence. This indicates that for an individual dendron molecule, a single accepter is not strong enough to quench the luminescence. In addition, charge transfer in solid samples of the dendrons is inter-molecular charge transfer.
Figure 7.12: Photoluminescence of the donor and the three dendrons in chloroform (CHCl$_3$) solutions.
7.4 Time resolved fluorescence measurement

In the previous section, we describe charge transfer between the donor functional groups and the accepter functional groups by comparing the photoluminescence spectra of the donor and the three dendrons. We have observed the strong inter-molecular charge transfer in solid dendron samples. However, we haven’t checked charge transfer of an individual dendritic molecule and we expect intra-molecular charge transfer from the donor functional group to the accepter functional group in an individual dendron. To check this, time-resolved fluorescence measurements are carried out for solutions of the dendrons and the donor. For the donor, we have strong luminescence peaks around 650 nm and 730 nm and the dendrons have similar luminescence.

Figure 7.13 is the schematic setup for time resolved fluorescence measurement. Photon Technology International’s Easy Life LS is the instrument used in this measurement and its time resolution is as low as 100 picoseconds. An excitation LED has a pulse width of approximately 1.5 nanosecond, which is comparable to the fluorescence lifetimes of the donor and the dendrons. Thus, the resultant fluorescence is a convolution of the excitation LED pulse and the decaying response.

Consider that we have only one fluorescence decaying process. Resultant fluorescence intensity function, $O(t)$, can be expressed as

$$O(t) = \int_{-\infty}^{t} I(\tau) \eta e^{-\kappa(t-\tau)} d\tau$$ (7.1)

where $\kappa$ is the reciprocal of decaying time, $\eta$ is the fluorescence efficiency, and $I(\tau)$ is the excitation beam time profile. If we assume that $I(t)$ has a Gaussian profile,

$$I(t) = I_0 e^{-t^2/\sigma^2}$$ (7.2)
then, we can manipulate above two equations to obtain the following result.

\[
O(t) = \int_{-\infty}^{t} I(\tau) \eta e^{-\kappa(t-\tau)} d\tau \\
= I_0 \eta \int_{-\infty}^{t} e^{-\frac{\tau^2}{\sigma^2}} e^{-\kappa(t-\tau)} d\tau \\
= I_0 \eta \int_{-\infty}^{t} e^{-\left(\frac{\tau}{\sigma} - \kappa \sigma/2\right)^2} e^{-\kappa t + \kappa^2 \sigma^2/4} d\tau \\
= I_0 \eta e^{-\kappa t + \kappa^2 \sigma^2/4} \int_{-\infty}^{t} e^{-\left(\frac{\tau}{\sigma} - \kappa \sigma/2\right)^2} d\tau \\
= I_0 \eta e^{-\kappa t + \kappa^2 \sigma^2/4} \int_{-\kappa \sigma/2}^{t} e^{-\frac{(\tau/\sigma)^2}{2}} d\tau \\
= I_0 \eta e^{-\kappa t + \kappa^2 \sigma^2/4} \int_{-\kappa \sigma/2}^{t} e^{-\frac{(\tau/\sigma)^2}{2}} d\tau
\]

When time elapses to \( t > \kappa \sigma^2/2 \), then, the above equation becomes

\[
O(t) = \frac{1}{2} O_0 (1 + \text{Erf}(t/\sigma - \kappa \sigma/2)) e^{-\kappa t}
\]

(7.3)

where

\[
O_0 = \frac{4}{\sqrt{\pi}} I_0 \eta \sigma e^{\kappa^2 \sigma^2/4}
\]

(7.4)

and \text{Erf} is an error function.

With multiple decaying channels, the above equation is also written as

\[
O(t) = \sum_{n=1}^{N} \frac{1}{2} O_0^n (1 + \text{Erf}(t/\sigma - \kappa_n \sigma/2)) e^{-\kappa_n t}
\]

(7.5)

When the argument of the error function is large, multiplier of the above decaying function is almost constant. Criteria of this condition is

\[
t > 3\sigma + \kappa \sigma^2/2
\]

(7.6)

If decaying time is larger than input excitation pulse width, this criteria is simply

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Thus, Eq. 7.3 is simply

$$O(t) \simeq O_0 e^{-\kappa t} = O_0 e^{-t/\tau_0} \quad (7.8)$$

where $\tau_0$ is the decay time constant.

Total emission energy ($E_{\text{emission}}$) is approximated as

$$E_{\text{emission}} = \int_0^\infty O(t)dt \simeq O_0 \int_0^\infty e^{-t/\tau_0}dt = O_0 \tau_0 \quad (7.9)$$

In the measurement of fluorescence lifetimes, three different solvents (chloroform, tetrahydrofuran, and toluene) are used for each donor and dendron. Because there are two fluorescent peaks (about 650 nm and 730 nm), measurements for both peaks and for each peak are carried out.
Figure 7.14: Time-resolved fluorescence of dilute solutions of the donor, Dendron A, B, and C in tetrahydrofuran (THF, C₄H₈O) with an excitation LED of λ = 460 nm. An emission filter, transparent at 630 nm < λ < 2200 nm, is used.
Figure 7.15: Time-resolved fluorescence of dilute solutions of the donor, Dendron A, B, and C in toluene ($C_6H_5CH_3$) with an excitation LED of $\lambda = 460$ nm. An emission filter, transparent at $630 \text{ nm} < \lambda < 2200 \text{ nm}$, is used.
Figure 7.16: Time-resolved fluorescence of dilute solutions of the donor, Dendron A, B, and C in chloroform (CHCl₃) with an excitation LED of λ = 460 nm. An emission filter, transparent at 630 nm < λ < 2200 nm, is used.
Figure 7.17: Time-resolved fluorescence of dilute solutions of the donor, Dendron A, and C in chloroform (CHCl₃) with $\lambda = 460$ nm excitation LED. The emission filters are $630 \, \text{nm} < \lambda < 670 \, \text{nm}$ (top) and $\lambda > 760 \, \text{nm}$ (bottom).
Figure 7.18: Time-resolved fluorescence of dilute solutions of the donor, Dendron A, and C in tetrahydrofuran (C$_4$H$_8$O) with $\lambda = 460$ nm excitation LED. The emission filters are $630 \text{ nm} < \lambda < 670 \text{ nm}$ (top) and $\lambda > 760 \text{ nm}$ (bottom).
Figure 7.19: Time-resolved fluorescence of dilute solutions of the donor, Dendron A, and C in toluene (C₆H₅CH₃) with $\lambda = 460$ nm excitation LED. The emission filters are $630 \text{ nm} < \lambda < 670 \text{ nm}$ (top) and $\lambda > 760 \text{ nm}$ (bottom).
Figure 7.20: Time-resolved fluorescence of solid film of the donor with $\lambda = 460$nm excitation LED. The emission filters are $630 \text{ nm} < \lambda < 670 \text{ nm}$ (650nm center) and $\lambda > 760 \text{ nm}$ (bottom).

Figures 7.14, 7.15, and 7.16 are plots of fluorescence from two peaks for the donor, and the three dendrons using an emission filter of $\lambda > 630 \text{ nm}$. We observe that the lifetimes of the dendrons are shorter than that of the donor, thus, the accepter functional groups in the dendrons play important role in fluorescence lifetimes. Due to the Zinc atom in Dendron B, the fluorescent lifetime in Dendron B is much shorter, which is general for metallic porphyrin molecules due to the strong inter-system crossing by high-ordered orbitals in the metals. The dependence of environmental solvents is also a factor to determine lifetimes, but this is a minor factor than the presence of the accepter functional groups.
Table 7.1: Lifetimes of fluorescence ($\lambda > 630$ nm) for the donor and three dendrons. Excitation LED wavelength is 460 nm.

<table>
<thead>
<tr>
<th>material \ solvent</th>
<th>Chloroform</th>
<th>Tetrahydrofuran</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Donor</td>
<td>8.3 ns</td>
<td>9.3 ns</td>
<td>10.2 ns</td>
</tr>
<tr>
<td>Dendron A</td>
<td>2.9 ns</td>
<td>8.1 ns</td>
<td>9.3 ns</td>
</tr>
<tr>
<td>Dendron B</td>
<td>0.7 ns</td>
<td>1.0 ns</td>
<td>1.1 ns</td>
</tr>
<tr>
<td>Dendron C</td>
<td>3.9 ns</td>
<td>6.0 ns</td>
<td>7.0 ns</td>
</tr>
</tbody>
</table>

Figures 7.17, 7.18, and 7.19 show lifetimes for each fluorescent peak. There is little difference of lifetimes in both fluorescent peaks. Thus, vibration is not a important factor for the fluorescence lifetime.

When lifetimes of Dendron A and C are compared, in the solutions of toluene and tetrahydrofuran, Dendron A’s lifetimes are longer although Dendron A has shorter linkage than Dendron C. However, due to the difference of structures between Dendron A and Dendron C, charges transfer through $\pi$-stacking between the donor and the accepter functional groups is present because Dendron C has shorter distance between the donor and the accepter functional groups.

But for solutions in chloroform, Dendron A has shorter lifetime than Dendron C. Thus, structure of Dendron A is believed to change like Dendron C, i.e. the donor functional groups are folded toward the accepter functional group. In this case, charge transfer through the linkage should be considered to support the shorter lifetime of Dendron A.

In the solid form of the donor (Figure 7.20), lifetimes at both peaks are much shorter than those of the donor in solution. Thus, the neighboring donor molecules promote additional interaction to shorten the fluorescence lifetime.
<table>
<thead>
<tr>
<th>material</th>
<th>peak (nm)</th>
<th>Chloroform</th>
<th>Tetrahydrofuran</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Donor</td>
<td>650 nm</td>
<td>7.7 ns</td>
<td>9.0 ns</td>
<td>9.9 ns</td>
</tr>
<tr>
<td></td>
<td>760 nm</td>
<td>7.6 ns</td>
<td>9.8 ns</td>
<td>10.7 ns</td>
</tr>
<tr>
<td>Dendron A</td>
<td>650 nm</td>
<td>2.6 ns</td>
<td>8.2 ns</td>
<td>8.7 ns</td>
</tr>
<tr>
<td></td>
<td>760 nm</td>
<td>2.8 ns</td>
<td>8.0 ns</td>
<td>8.9 ns</td>
</tr>
<tr>
<td>Dendron C</td>
<td>650 nm</td>
<td>3.9 ns</td>
<td>5.6 ns</td>
<td>7.0 ns</td>
</tr>
<tr>
<td></td>
<td>760 nm</td>
<td>4.0 ns</td>
<td>6.2 ns</td>
<td>6.8 ns</td>
</tr>
</tbody>
</table>

Table 7.2: Lifetimes at two fluorescence peaks for the donor, Dendron A, and C. Excitation LED wavelength is 460 nm. Note that the solid donor lifetime is 1.9 ns at 650 nm, and 4.0 ns at 760 nm.

### 7.5 Fabrication of simple photovoltaic devices

Photovoltaic cells in this thesis are fabricated in the structure of simple photovoltaic cells (anode/active layer/cathode). Indium tin oxide (ITO) glass with work function energy around 4.8 eV is used as an anode layer, which is properly cleaned in inorganic and organic solvents with ultrasonication. Hole transport layers of AI 4083 (one of Baytron P’s from Bayer™) without any modification of the solution are spin-coated on ITO substrates at 2,000 rpm for 60 seconds. The AI 4083 solution is a dispersion of polyethylenedioxythiophene/polystyrenesulfonic acid. Thus, filtration of this solution with 0.45 µm syringe filters is carried out before spin-coating. Immediately after the spin-coating of AI 4083, the hole transporting layers are baked on a hot plate of 200 °C for 60 seconds.

Active layers are spin-coated from solutions of the three dendrons, the donor, and the acceptor. Solvents of chloroform (CHCl₃) and tetrahydrofuran (THF, C₄H₈O) are used. For Dendron A, chloroform is used while for Dendron B and C, tetrahydrofuran is used due to solubility. For the donor and the acceptor, both solvents are used. Thick
active layer is approximately 300 nm thick and thin active layer is approximately 50 nm thick, which is controlled by changing the concentration of the solutions. Cathode layers are made of aluminum, generated by careful and slow evaporation at a rate from 1 to 2 Å/sec to a thickness of around 300 Å.

7.6 Methods of photocurrent measurements

Photovoltaic devices with active layers of donor only, accepter only, Dendron A, B, and C are measured under monochromatic light from a seventy five Watt Xenon lamp through a monochromator to obtain IV characteristic curves (Figure 7.21 (a)). This instrument is a part of the Photon Technology International’s Quanta Master Series, QM1. A sourcemeter (Keithley Instrument, Model 2400) serves as a voltage source and a current meter with current accuracy of 1 pA.

The temperature dependence of the short circuit currents and open circuit voltages is also measured by using a helium refrigerator (CTI-Cryogenics Model 22). In this measurement, a halogen lamp is used for the incident light source on the photovoltaic cells.

It turns out that considerable shunt currents appear in the photovoltaic cells. A method to obtain pure photocurrents is required to characterize photovoltaic devices. Figure 7.21 (b) is a schematic setup for taking pure optical photocurrents. The photocurrents are modulated with the same frequency as the optical chopper (Stanford Research System, SR540). A halogen lamp is used for an incident light source and CVI’s Digikrom 240 monochromator with 2000 µm slit width is used to obtain monochromatic incident light. An analog lock-in-amplifier (Stanford Research System, SR530) is used for the lock-in-amplification of the modulated photocurrents.
Figure 7.21: Experimental setups for IV characteristic curves of photovoltaic cells (a), and pure photocurrents by using optical modulations (b).
Notch filters for 60 Hz and 120 Hz are used for filtering improper signals from the environments. To avoid signals at multiples of 60 Hz, a modulation frequency of 50 Hz is selected and the integration time of the lock-in-amplifier is about 3 seconds in order to stabilize output signals.

7.7 Results

Plots in Figure 7.22 are the IV characteristics of the dendron photovoltaic cells under monochromatic incident light. Wavelengths of the incident light are chosen to be at the absorption peaks of the dendrons. The active areas of the photovoltaic cells are approximately 2 mm by 2 mm. In these plots, we can notice that the current at the Soret band is not large considering its strong absorption. Although the absorption peaks of the Q bands are much smaller than the absorption peak at the Soret band, the IV currents at the Q bands are larger than that in the Soret band. However, the photovoltaic cell made of Dendron C does not yield high photocurrents.

Filled factors are approximately 0.25 because the curves are almost linear in the quadrant of positive voltage-negative current. The open-circuit voltages are approximately 1.0 V. This is from the work function difference between the cathode (Aluminum 4.2 eV) and the anode (ITO 4.8 eV) and built-up potentials from molecular dipoles of the dendrons. The IV curves have hysteresis effects. Power conversion efficiencies for these photovoltaic cells are small, less than 0.01 percent.

Figures 7.23, 7.24, and 7.25 show IV characteristic curves for forward and backward scannings and the plots to check space-charge-limited currents (SCLC). The scanning speed is approximately 10 mV/sec. First, there is an open-circuit voltage difference between the forward and backward IV curves under light illumination.
Figure 7.22: IV characteristic curves (scanned in negative direction) of Dendron A, Dendron B, and Dendron C photovoltaic cells. Note that Soret band current is not high despite strong absorption.
Figure 7.23: IV characteristic curves (top) and space charge limited currents of photovoltaic cell (bottom) with thick Dendron A layer. Left plots scan bias voltage in positive direction and right plots scan bias voltage in negative direction. For top plots, y values are absolute values of current. For bottom plots, x values are \((V - V_{bi})^2\) when \(V > V_{bi}\) and \(- (V - V_{bi})^2\) when \(V < V_{bi}\).

However, there is a small difference between the dark currents. One possible reason is that dendrons have large dipolar moments under light illumination. Dipolar moments can modify interface properties in the devices [97]. Except for Dendron C, net dipole moments are created from the accepters to the donors. Because the donors of Dendron C are folded into the accepter, net dipolar moment of Dendron C is zero by canceling out each dipole moment from the accepter to the donor. This
Figure 7.24: IV characteristic curves (top) and space charge limited currents of photovoltaic cell (bottom) with thick Dendron B layer. Left plots scan bias voltage in positive direction and right plots scan bias voltage in negative direction. For top plots, y values are absolute values of current. For bottom plots, x values are $(V - V_{bi})^2$ when $V > V_{bi}$ and $-(V - V_{bi})^2$ when $V < V_{bi}$.

is proven in Figure 7.25 by small open-circuit voltage difference between the forward and backward IV curves.

From the plots to check space charge limited currents (the bottom plots in Figures 7.23, 7.24, and 7.25), IV curves have linear relations between $I$ and $V^2$ except the origins, which indicate charge transport by space charge limited currents (SCLC).

$$I \propto V^2$$  \hspace{1cm} (7.10)
Figure 7.25: IV characteristic curves (top) and space charge limited currents of photovoltaic cell (bottom) with thick Dendron C layer. Left plots scan bias voltage in positive direction and right plots scan bias voltage in negative direction. For top plots, y values are absolute values of current. For bottom plots, x values are \((V - V_{bi})^2\) when \(V > V_{bi}\) and \(- (V - V_{bi})^2\) when \(V < V_{bi}\).

The open circuit voltage for each IV curve is used as a built-in-potential. Polarities of \((V - V_{bi})\) on the photovoltaic cells also affect charge transport. In voltages above built-in potentials, slopes for forward and backward scannings are different, shown in Figures 7.23 and 7.24. These differences of the slopes come from the injections of different charge carriers.
Figure 7.26: IV characteristic curves (top) and space charge limited currents of photovoltaic cell (bottom) with thin Dendron A layer. Left plots scan bias voltage in positive direction and right plots scan bias voltage in negative direction. For top plots, y values are absolute values of current. For bottom plots, x values are \((V - V_{bi})^2\) when \(V > V_{bi}\) and \(- (V - V_{bi})^2\) when \(V < V_{bi}\).

Figures 7.26, 7.27, and 7.28 show IV characteristic curves for thinner dendron layered cells than the previous cells. The open-circuit voltage differences are not as great as in the thick Dendron A or Dendron B photovoltaic cells. One reason is that active layer is so thin that it cannot accumulate dipolar moments of the dendrons. Further evidence is that the plots of checking \(I \propto V^2\) do not show linear relationships. They are similar to diode-like curves. Thin active layers do not contribute much to the potential accumulation.
Figure 7.27: IV characteristic curves (top) and space charge limited currents of photovoltaic cell (bottom) with thin Dendron B layer. Left plots scan bias voltage in positive direction and right plots scan bias voltage in negative direction. For top plots, y values are absolute values of current. For bottom plots, x values are $(V - V_{bi})^2$ when $V > V_{bi}$ and $-(V - V_{bi})^2$ when $V < V_{bi}$.

In brief, the hysteresis effects of IV curves between forward and backward scanings are mostly due to the accumulation of dipolar moments in the dendron layers.

Figure 7.29 shows the temperature dependence of open circuit voltages and short circuit currents for Dendron A and B photovoltaic cells. As expected, open circuit voltages do not change significantly under variation of temperature, while photocurrents (short circuit currents) have a strong dependence on temperature. Because
Figure 7.28: IV characteristic curves (top) and space charge limited currents of photovoltaic cell with thin Dendron C layer. Left plots scan bias voltage in positive direction and right plots scan bias voltage in negative direction. For top plots, y values are absolute values of current. For bottom plots, x values are $(V - V_{bi})^2$ when $V > V_{bi}$ and $-(V - V_{bi})^2$ when $V < V_{bi}$.

the change of short circuit current does not depend on the wavelength but on the temperature, the charge transport is phonon assisted transport.

Due to hysteresis in photocurrents, incident light modulation is used to obtain the pure photocurrents. Three different dendrons provide different photocurrent spectra as shown in Figures 7.30 and 7.31. Comparing Dendron A and Dendron C photovoltaic cells, significant differences in the Q band current for positive bias are observed
Figure 7.29: Temperature dependence of open circuit voltages and short circuit currents for Dendron A and B photovoltaic cells. These data are obtained under monochromatic light from a halogen lamp.
(wavelength from 500 nm to 600 nm) in both amplitude and phase. Comparing Dendron A and Dendron B photovoltaic cells, both Q band photocurrents are weak, and phases are similar for positive bias. However, singlet states without a vibration mode in the Dendron B cell is also weak compared with Dendron A cell. Therefore, the Dendron B cell has significant current only for negative bias.

To understand the rolls of the donor and the accepter, two kinds of photovoltaic cells made with donor only and accepter only are prepared and compared. For the donor only cells, significant photocurrents in the Soret and the Q bands appear, shown in Figure 7.32. There are strong photocurrents for positive bias voltages, which are very different from the photocurrents in the Dendron A and B photovoltaic cells. Thus, there is no dependence of bias polarity in the donor only photovoltaic cells. Positions of peaks are not much affected by the choice of solvents. However, the widths of peaks in tetrahydrofuran are much wider than those in chloroform. Thus, the donor films prepared from tetrahydrofuran based solution have stronger mutual interaction than those from chloroform based solution.

For the accepter, photocurrent is asymmetric in the bias polarity. For negative bias and bias lower than 1.0 V, there is significant photocurrent around its absorption wavelength (around 390 nm). At high positive voltage, there is extremely small photocurrent around 390 nm. There are extra peaks in 440 nm and 660 nm from the accepter film prepared from chloroform based solution. These two peaks are different from the peak at 390 nm in the phases for positive bias. In short, the photocurrent in the accepter only cell strongly depends on the polarity of the bias voltage.

For the bias-wavelength spectra in Figures 7.30, 7.31, 7.32, and 7.33, the photocurrent spectral peak shifts are observed for zero vibrational energy singlet states,
Figure 7.30: Modulated photocurrent amplitude spectra of photovoltaic cells based on Dendron A (top), Dendron B (middle), and Dendron C (bottom). Red indicates higher photocurrent.
Figure 7.31: Modulated photocurrent phase spectra of photovoltaic cells based on Dendron A (top), Dendron B (middle), and Dendron C (bottom). Red indicates positive current and blue indicates negative current. Zero current has a phase of approximately 50 degree.
Figure 7.32: Modulated photocurrent amplitude (left) and phase (right) spectra of the photovoltaic cells based on donor only (tetraphenylporphyrin). Solvents to dissolve the donor are tetrahydrofuran (top) and chloroform (bottom).
Figure 7.33: Modulated photocurrent amplitude (left) and phase (right) spectra of the photovoltaic cells based on accepter only (naphthalenediimide). Solvents to dissolve the accepter are tetrahydrofuran (top) and chloroform (bottom).
$S_1$ (the lowest Q) and $S_2$ (Soret). Figure 7.34 shows noticeable shifts of the photocurrent peaks by changing bias voltage. At low (negative) bias voltages, the peak related to Soret band is located at 452 nm for the Dendron A cell and at 443 nm for the Dendron C cell. The peaks for the $S_1$ states are located at 655 nm for both cells. At high (positive) bias voltages, the peak related to the Soret band is slightly shifted to 457 nm for the Dendron A cell. The peak related to the $S_1$ level is shifted to 670 nm for the Dendron A cell and 665 nm for the Dendron C cell. Around zero bias voltage, it is difficult to measure photocurrent peaks. For the peaks of the Q-band photocurrents, there are no significant shifts.

### 7.8 Discussion for charge transfers in dendrons

In the photoluminescence spectra shown in Figures 7.7, 7.8, 7.9, 7.10, and 7.11, it is already indicated that there should be charge transfer (inter-molecular charge transfer) in the systems due to the photoluminescence quenching around the lowest $S_1$ energy states. The lifetime measurement results prove that there is charge transfer from the donor to the accepter functional groups within a dendritic molecule (intra-molecular charge transfer). Thus, both types of charge transfer are present in the dendron molecules.

In Figure 7.11, very weak but noticeable photoluminescence peaks are also located at a few vibrational levels above the $S_1$ state in the Dendron C film. The origin of the weak Q band photoluminescence in Dendron C is explained by poor charge transfer through extra ortho-benzoic linkage. Some of the excited charges cannot go to the accepter, so there is an internal relaxation of energy down to the vibrational energy
Figure 7.34: Peak shifts in photocurrent spectra from Dendron A (top) and Dendron C (bottom) photovoltaic cells.
levels in Q bands, then an additional relaxation provides weak Q band photoluminescence peaks.

For the bias-wavelength photocurrent spectra shown in Figures 7.30, 7.31, 7.32, and 7.33, photocurrent spectra from Dendron C photovoltaic cell are similar to those from donor only photovoltaic cells, both in amplitude and phase. Another remarkable fact is photocurrents in the Q bands are strongly dependent on the photocurrents of the accepter. Figure 7.33 shows that there is no photocurrent at positive bias and significant current at negative bias for the accepter only cell. Similar features are observed in Dendron A photocurrents. Thus, the accepters in Dendron A play the role of trapping photo-generated electrons in the Q bands in high positive bias, while they serve as transporting sites in negative bias. However, in Soret band and lowest S$_1$ states, there are still significant photocurrents, so direct inter-molecular charge transfer process is more dominant than the charge transfer via the accepter groups in the dendrons.

For Figure 7.34, the shifts of photocurrent peaks by changing bias voltages are observable for the Soret band and the lowest Q band in the Dendron A photovoltaic cell. The Dendron C photovoltaic cell also has similar peak shifts. The high energy Q band peaks in both Dendron A and C cells do not shift their peaks by changing bias voltages. This can also be explained by the difference of photo-generated charges from Soret and lowest Q band, and from high energy Q bands.

Figure 7.35 summarizes the charge transport both in solution and solid states. When an individual molecule is considered (dendron in solution), intra-molecular charge transfer is proposed. This intra-molecular charge transfer has two kinds of charge transfer, inter-functional group charge transfer via $\pi$-stacking and the charge
transfer through the linkages. However, when dendrons form a solid film, inter-
molecular interaction dominates, but the charge transfer is band-selective. Due to the 
switching role of the accepter functional groups, high-energy Q band photoelectrons 
generally transport via the accepter functional groups, while the Soret band and the 
lowest Q band photoelectrons can transport directly between dendritic molecules.

Figure 7.35: Schematic illustrations of the charge transport of dendron in solid and solution states.
CHAPTER 8

SUMMARY AND PROSPECT

Polymeric and organic systems have exhibited many features which conventional inorganic materials have achieved. However, transport of charges by electric or optical fields in organic material requires different models, such as, charge transport in disordered systems.

Poly(3,4-ethylenethiophene) and dendrons with tetraphenylporphyrin and naphthalenediimide are studied by making thin-film field effect transistors and photovoltaic cells respectively. Device characterizations via IV curves, fluorescence measurements, and fluorescence life time measurements are utilized in this thesis.

Although a poly(3,4-ethylenethiophene) film prepared in this thesis is very conductive compared with other organic or polymer semiconductors, field effects are observed and many conventional features of field effect transistors are realized such as drain-source current modulations by gate electric field and drain-source saturation currents. In addition, electric circuit applications such as inverting amplifiers and current limiters are shown to check device operation. Switching on (i.e. drain-source current is zero at high gate voltage) is relatively fast (less than 0.5 second) while switching off time is relatively long (100’s seconds). This is because it is hard to separate the ions from hopping sites in the polymers.
One of the possible solutions for this problem is to use double gate field effect transistors where two gate electrodes sandwich an active channel. In this case, the gate voltage swings from $-V_{G0}$ to $+V_{G0}$ instead of 0 to $+V_{G0}$ so that the switching-on and the switching-off times are same, which is similar to the experiment in Figure 5.4. However, the most important solution is to reduce the channel length and to create more ordered polymer.

Dendrons of tetraphenylporphyrin (charge donor) and naphthalenediimide (charge accepter) are used for photovoltaic devices. From the measurements of photoluminescences and lifetimes of the dendrons, both inter-molecular and intra-molecular charge transfers are present in the dendron systems. In the characterization of the photovoltaic cells, photocurrent at each absorption peak (Soret band or Q band) is observed. However, the photocurrents at the Soret band, at the lowest Q band, and the high-energy Q bands have different features. High energy Q-band photo-currents are closely related to the accepter functional groups in the dendrons. For positive bias in the photovoltaic cells, accepters serve as charge traps of the excited photo-electrons, and for negative bias, they serve as charge transporters. The photocurrents from the Soret band and the lowest Q band do not depend on the photocurrents of the accepter functional groups. Thus, direct charge transport between dendrons is proposed for these bands.

For good dendron photovoltaic cells in the future, there are many factors to be considered. Photovoltaic materials need to absorb light in visible spectral range as well as near infra-red spectral range. Thus, low bandgap organic/polymeric materials are necessary for this purpose. In addition, tandem photovoltaic cells can be considered [98]. Because inorganic semiconductors have bandgaps about 1.0 eV to
1.5 eV and organic semiconductors have higher bandgaps (larger than 2.0 eV), incorporation of both materials can cover almost all wavelengths in solar spectrum. For dendritic materials, generation number of dendrons, choice of donor and accepter functional groups, and design of linking functional groups are considered for more efficient photovoltaic cells.
APPENDIX A

DECONVOLUTION PROGRAM

This program is a C program which finds fluorescence lifetimes. We assume that there is only one fluorescence decay process. Raw data should have a proper y-offset (no constant term) that the result is in the form of

\[ F(t) = F_0 e^{-t/\tau} \]  \hspace{1cm} (A.1)

where \( \tau \) is a fluorescence lifetime.

// Deconvolution program coded by June Hyoung Park

#include <stdio.h>
#include <math.h>
#include <string.h>
#define DATA_NUM 201 // number of data

double data[DATA_NUM][3]; // time, excitation light, emission light
double input[DATA_NUM]; // excitation light will be copied here
double output[DATA_NUM]; // fitting curve
double time_interval;

double deconvolution(double A1, double t1); // deconvolution integral

void main(void)
{
    FILE* fp; // a pointer to a file

    // dummy variables
int i, temp_i1;
double temp_d1;
float temp_f1, temp_f2, temp_f3;
char filename[255];
char temp_string[255];

// magnitude and lifetime
double A1, t1;
double dA1, dt1;
double A_resolution, t_resolution;
double error[4];
double error_min; // for a minimum error value

// read data from file
printf("\nInput your file : ");
scanf("%s", filename);
strcpy(temp_string, filename);
strcat(temp_string, ".txt");
fp = fopen(temp_string, "r");
for (i = 0; i < DATA_NUM; i++)
{
    fscanf(fp, "%f\t%f\t%f\n", &temp_f1, &temp_f2, &temp_f3);
data[i][0] = double(temp_f1);
input[i] = data[i][1] = double(temp_f2);
data[i][2] = double(temp_f3);
    printf("%f\t%f\t%f\n", data[i][0], data[i][1], data[i][2]);
}
fclose(fp);

// time interval
time_interval = data[1][0] - data[0][0];

// normalize excitation beam profile to make a delta function
temp_d1 = 0.;
for (i = 1; i < DATA_NUM; i++)
    temp_d1 += ( 0.5 * (data[i-1][1] + data[i][1]));
temp_d1 *= time_interval;

for (i = 0; i < DATA_NUM; i++)
    data[i][1] /= temp_d1;

// input parameters
printf("\nInput A1:");
scanf("%f", &temp.f1);
A1 = double(temp.f1);

printf("Input t1:");
scanf("%f", &temp.f1);
t1 = double(temp.f1);

dA1 = A1 / 10.;
dt1 = t1 / 10.;

printf("Input Amplitude resolution:");
scanf("%f", &temp.f1);
A_resolution = double(temp.f1);

printf("Input time resolution:");
scanf("%f", &temp.f1);
t_resolution = double(temp.f1);

// initial calculation
error_min = deconvolution(A1, t1);

// begin while loop
while(dA1 > A_resolution || dt1 > t_resolution)
{
// computation of errors
error[0] = deconvolution(A1 - dA1, t1);
error[1] = deconvolution(A1 + dA1, t1);
error[2] = deconvolution(A1, t1 - dt1);
error[3] = deconvolution(A1, t1 + dt1);

// find minimum error
temp_d1 = error[0]; // minimum error
temp_i1 = 0; // minimum error point
for (i = 1; i < 4; i++)
{
  if (error[i] < temp_d1)
  {
    temp_i1 = i;
    temp_d1 = error[i];
  }
}

if (temp_d1 < error_min)
{ switch(temp_i1) // update minimum error point 
  { case 0:
    A1 = A1 - dA1; t1 = t1; break;
  case 1:
    A1 = A1 + dA1; t1 = t1; break;
  case 2:
    A1 = A1; t1 = t1 - dt1; break;
  case 3:
    A1 = A1; t1 = t1 + dt1; break;
  }

  error_min = temp_d1; // update minimum error value
  if (A1 < 0.) A1 = dA1;
  if (t1 < 0.) t1 = 1.1 * dt1;
  if (t1 > 1000.) break;
}
else // reach local minimum error point
{
  // find maximum error
  temp_d1 = error[0]; // maximum error
  temp_i1 = 0; // maximum error point
  for (i = 1; i < 4; i++)
  {
    if (error[i] > temp_d1)
      temp_i1 = i;
  }
  switch(temp_i1)
  {
    case 0:
    case 1:
      dA1 /= 2.; break;
    case 2:
    case 3:
      dt1 /= 2.; break;
  }
}
printf("\n%f, %f, error = %f, dA1 = %f, dt1 = %f",
    A1, t1, error_min, dA1, dt1);
}

error_min = deconvolution(A1, t1);
// write result in a file
strcpy(temp_string, filename);
strcat(temp_string, "_result.txt");
fp = fopen(temp_string, "w");
fprintf(fp, "Program version 200612291429\n");
fprintf(fp, "A1 = %f, t1 = %f\n", A1, t1);
fprintf(fp, "error = %e, standard deviation per point = %f\n",
       error_min, sqrt(error_min / float(DATA_NUM)));
fprintf(fp, "A resolution = %e, t resolution = %e, ",
       A_resolution, t_resolution);
fprintf(fp, "dA = %e, dt = %e", dA1, dt1);
close(fp);

// write data profile
strcpy(temp_string, filename);
strcat(temp_string, "_curve.txt");
fp = fopen(temp_string, "w");
fprintf(fp, "Time\tInput\tData\tFitting\n");
for (i = 0; i < DATA_NUM; i++)
   fprintf(fp, "%f\t%f\t%f\t%f\n",
           data[i][0], input[i], data[i][2], output[i]);
close(fp);

double deconvolution(double A1, double t1)
{
   int i, x;
   double temp_d1;

   for (i = 0; i < DATA_NUM; i++)
   {
      temp_d1 = 0.;
      for (x = 0; x < i; x++) // simple Euler integration
      {
         temp_d1 += (0.5 * (data[x][1] * A1 *
                        exp(-(data[i][0] - data[x][0])/t1)
                        + data[x+1][1] * A1 *
                        exp(-(data[i][0] - data[x+1][0])/t1)));
      }
      output[i] = temp_d1 * time_interval;
   }
}
// calculate error using least square method
temp_d1 = 0.;
x = 0;
for (i = 0; i < DATA_NUM; i++)
{
    temp_d1 +=((output[i] - data[i][2])*(output[i] - data[i][2]));
}
return temp_d1;
}
BIBLIOGRAPHY


