Abstract

Fluorescence decay traces of APFO3 (Poly [2,7-(9,9-dioctylfluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3-benzothiadiazole)]), 4-1 APFO3:PCBM blend and 1-1 APFO3:PCBM blend have been observed. Delayed fluorescence decay traces are visible in both the APFO3:PCBM blends. This delayed fluorescence is because of intermediate emissive states that are created in APFO3:PCBM blends alone. Time Correlated Single Photon Counting (TCSPC), a time-resolved technique, is used to detect the fluorescence from these intermediate emissive states. The fluorescence life-times of the above emissions are measured to be ~4.45ns for the 4-1 APFO3:PCBM blend, and to be ~3.95ns for the 1-1 APFO3:PCBM blend, and these periods are smaller than the time-scale for geminate recombination of charges. Thus, these intermediate emissive states are not formed from the recombination of charges. All of the time-resolved experiments are performed within such an intensity range of laser beam, that only light intensity independent processes take place in the samples. Further, the samples are illuminated for 10hrs to study the degradation they undergo.

Popular Science

Polymer solar cells are a good alternative of silicon-based inorganic solar cells. A solar cell is a technology that converts sun-light into electricity. The part of solar cell that absorb sun-light is called active layer. In polymer solar cells, the active layer can be of three different types: single layered, double layered and bulk heterojunction. The single layered structure consists of polymer only. When polymer absorbs the sun-light, electrons are excited from the ground state to excited states of the polymer hence leaving behind holes in the ground state. The excited states' electrons still have strong columbic interaction with ground state's holes. These electron-hole pairs with strong columbic interaction are called excitons. The dissociation of excitons into free charge carriers is not sufficient in single layered structure so efficiency of solar cells is very less. Single layered structure is replaced with double layered structure which consists of a polymer layer and a layer of electron-accepting molecules. In this structure, the generated excitons are dissociated into free charge carriers at the donor-acceptor interface similar to silicon-based pn-junction. But excitons can travel within ~4-20ns therefore only those excitons that are generated close to donor-acceptor interface would be able to dissociate into free charge carriers and the remaining ones are lost. This problem is solved with bulk heterojunction structure where polymer and electron-accepting molecules are blended together on nano-structure scale. Therefore, for each generated exciton in the polymer there is an acceptor molecule hence all excitons dissociate into free charge carriers at donor-acceptor interface and efficiency of the cell increases remarkably.

When excitons dissociate into free charges, some of them are collected at their respective electrodes but most of them recombine with each others. If charges belonging to same exciton recombine then it is called geminate recombination otherwise it is called non-geminate recombination. Geminate recombination is a light intensity independent process and non-geminate recombination is a light intensity dependent process. Under solar illumination, only light intensity independent processes occur in polymer solar cells. It is supposed that dissociation of excitons into free charge carriers at donor-acceptor interface is not direct but some intermediate states are formed at donor-acceptor interface. Some charges may stay at intermediate states for nano-second time scale and then decay back to ground state so emission from intermediate states is obtained. This emission is very weak and in order to detect it a very sensitive technique is required.

Time correlated single photon counting technique is uses to detect the emission and to measure the life-time of intermediate states. It consists of laser diode, turning mirrors, filters and detector. Laser beam from laser diode is directed to incident on samples by using turning mirrors. Meanwhile the intensity of laser beam is reduced by using optical density filters to such an intensity range that only light intensity independent processes occur in samples. After the samples, an avalanche photo-diode is placed to detect the emission from the samples. Avalanche photo-diode is connected to a photon counter "PicoHarp" that collects the photons and their time of reach to draw the emission curves on the computer.

When emission curves are obtained, an analysis software "SymphoTime" is used for data acquisition and fitting. The fitting results give the life-time of intermediate states ~4ns.

Table of Contents

1. Introduction

Polymer solar cells are a good alternative to inorganic solar cells. They are usually made of conjugated polymers. A polymer solar cell's efficiency is a big challenge [1]. The basic working principle of polymer solar cells is, when light is absorbed, excitons are formed in the polymer. These excitons dissociate into charge pairs and current is obtained. The excitons can dissociate easily in the presence of an electron accepting molecule like fullerene and the solar cell's efficiency improves. When polymer is mixed with electron accepting molecules so that a bulk heterojunction (BHJ) structure is formed, then for each generated exciton in the polymer, there is an electron accepting molecule. Thus all excitons dissociate into charge pairs at the donor-acceptor interface and the polymer solar cell's efficiency increases remarkably in BHJ structures [2]. There is no clear picture about the dissociation of excitons at donor-acceptor interface in BHJ structures. But it is supposed that some intermediate emissive states are formed at the interface. To investigate these intermediate emissive states and measure the fluorescence life-time of these intermediate emissive states are the primary motive of this work.

Time correlated single photon counting (TCSPC) technique is used. TCSPC technique is quite sensitive in detecting even weak emissions from these intermediate emissive states. Meantime TCSPC is a time-resolved technique, so it can measure fluorescence life-time of the intermediate states. There are many processes occurring in polymer solar cells. Some of them are light intensity independent and some are light intensity dependent. Under the solar light intensity, only intensity independent processes occur in the cells [3]. Therefore we want to perform time-resolved experiments with such an intensity range of laser light, that only intensity independent processes occur in our samples. Polymer solar cells degrade under illumination and longer operational life-times of polymer solar cells are to be achieved [4]. Therefore another aim of our work is to study stability/degradation of our samples.

2. Material Description

2.1. Polymer solar cell

Polymer solar cells are also called plastic solar cells and are a relatively new technology. Solar cells convert solar energy into electricity. This class of solar cells is different from conventional solar cells because they are neither made of silicon nor any alloy material. As is clear from their name, polymer solar cells are made of polymers which will be discussed afterwards. Polymer solar cells are light-weight, biodegradable and inexpensive compared to silicon-based solar cells. The polymer makes them flexible, facilitating greater design possibilities and diverse applications. One of the main components used in the manufacturing of polymer solar cells is fullerene (a plastic based material) which is inexpensive and readily available so that the cells are easy to manufacture at the cost of approximately one-third of that of traditional silicon-based solar cell technology [5].

Although polymer solar cells are developing rapidly, there are still some issues that are not fully resolved. One such issue is the improvement of efficiency of polymer solar cells in converting the solar energy into electricity. Actually there are a number of processes occurring in polymer solar cells and in order to improve their efficiency, the study of all the processes is quite important. We will also try to observe one of those processes and try to describe it's importance.

Typically polymer solar cell devices have a layered structure. That part of the layered structure that absorbs the sun-light is called active layer. Like in conventional semiconductor solar cell devices, in polymer solar cells too, the active layer consists of donor and acceptor materials and the active layer is sandwiched between two electrodes. The basic principle of polymer solar cell, that is, the conversion of sun-light (photons) into electricity, can be described in four steps. When light is incident on the active layer, electrons are promoted from ground state to excited state and a hole is left behind in the ground state. This electron in excited state and hole in the ground state are not free from each other as they still have strong Coulombic interaction between them. In the second step, the electron-hole pair moves towards the donor-acceptor interface. This interface is the part where donor and acceptor materials meet each other. In the third step, electron-hole pairs are converted into free charge carriers at the interface. Finally, free charge carriers are collected at their respective electrodes. This whole basic principle is also shown in figure 1.
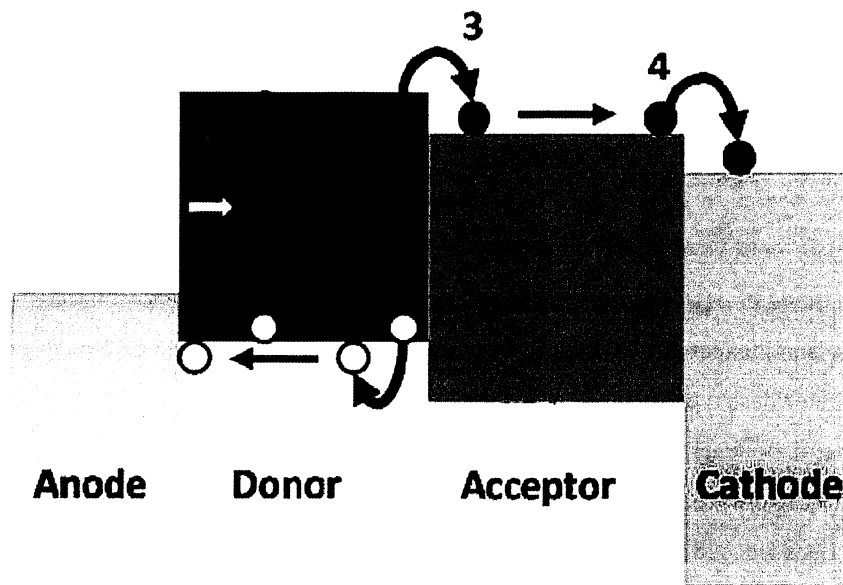
Figure 1. Schematic illustration of basic principle of polymer solar cell [6].

2.2. Bulk-heterojunction

The active layer of polymer solar cells can be designed in three different ways. It can be a single layer, a double layer or a bulk-heterojunction as shown in the figure 2. In the beginning, polymer solar cells had single layered structures in which electron-hole pairs were separated at the interface between the active layer and the electrode. But such a structure does not support efficient charge separation. Hence single layered structure was replaced by double layered structure (bilayer heterojunction) in which donor and acceptor materials are brought together to form a heterojunction, just like the pn-junction in silicon-based solar cells. But even in double layered structures, only those electron-hole pairs that are generated in the region close to the donor-acceptor interface are converted into free charges, while the pairs generated in the regions away from the interface are unable to reach the interface and hence remain unconverted. This means a large amount of light (photons) is wasted. The breakthrough came with bulk-heterojunction structures in which donor and acceptor are mixed in bulk; the donor-acceptor interface is extended to the whole of the active layer and all generated electron-hole pairs can reach the interface. Therefore bulk-heterojuction structure supports sufficient charge separation and the collection of charges at the electrodes is increased.
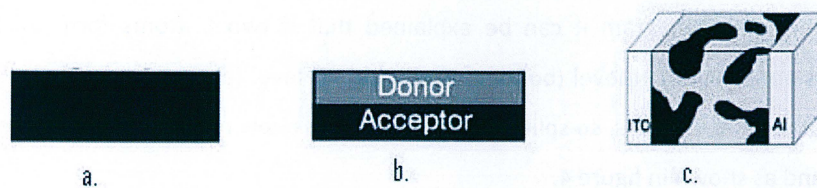
a.　　　　　b.　　　　　c.

Figure 2. Different designs of active layers (a) Single layered, (b) Bilayer and (c) Bulk-heterojunction [6].

2.3.　Conjugated Polymers

Polymer solar cells are made up of conjugated polymers, having a chain of alternative single and double carbon-carbon bonds as shown in figure 3a. A carbon atom has 6 electrons and the electronic configuration is $1S^2 2S^2 2P^2$. When two C-atoms interact with each other an electron from 2S-orbital is promoted to vacant 2P-orbital and the electronic configuration becomes $2S^1 2p_x^1 2p_y^1 2p_z^1$. Now these valence orbitals don't form the bond separately but rather are mixed together. If all four orbitals are mixed together then it is called Sp^3-hybridization. But in conjugated polymers the alternative single and double C-bonds are because of Sp^2-hybridization in which only $2S^1 2p_x^1 2p_y^1$ orbitals are mixed together, leaving $2p_z^1$ orbital un-hybridized. The Sp^2-hybridized orbitals of each atom lie linearly and form σ-bond with the Sp^2-hybridized orbitals of another C-atom. But $2p_z^1$-unhybridized orbitals lie perpendicularly and form another kind of bond called π-bond with other C-atoms[7]. Thus the π-bond causes the delocalization of electrons along the polymer chain as shown in the figure 3b.
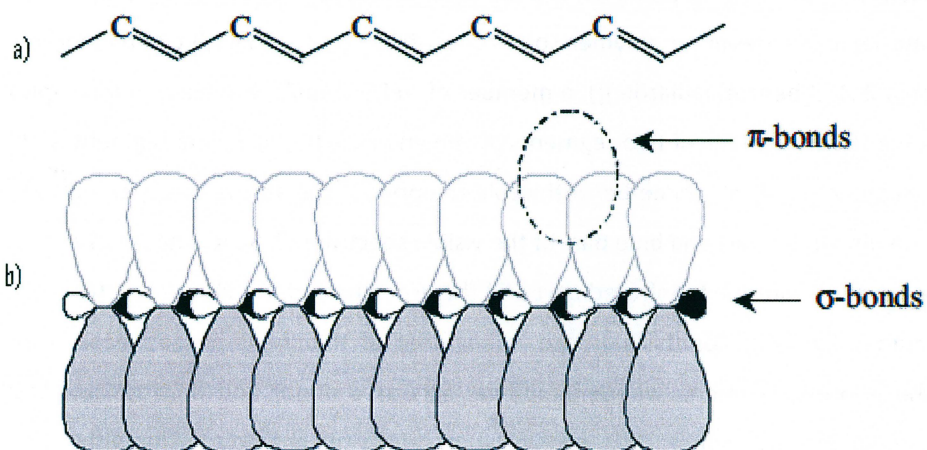

Figure 3. The alternative single and double bonds in conjugated polymer a) and formation of π-bond b).

In terms of energy level diagram it can be explained that if two C-atoms form a bond, then their molecular levels are split into π-level (bonding-level) and π*-level (anti-bonding level). But the polymer chain consists of several C-atoms, so splitting of molecular orbitals results in energy bands known as π-band and π*-band as shown in figure 4.
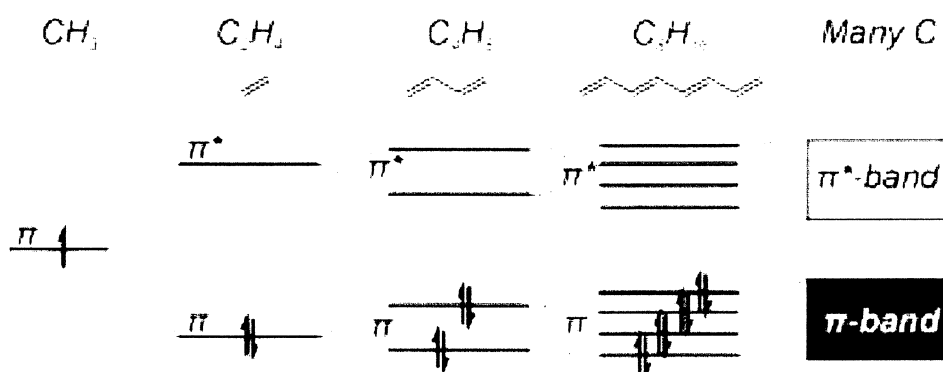

Figure 4. Splitting of molecular levels into bonding and anti-bonding levels [8].

The π-band is called valance band or highest occupied molecular orbital (HOMO) and π*-band is called conduction band or lowest un-occupied molecular orbital (LUMO). The energy gap between HOMO and LUMO is called band gap. The band gaps of conjugated polymers cover whole range from infrared to ultraviolet region [9].

2.4. APFO3

Alternating polyfluorene copolymers (APFOs) is a family of conjugated polymers that is commonly used as a donor material in the design of polymer solar cells. APFO3 (Poly [2,7-(9,9-dioctylfluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3-benzothiadiazole)]), a member of APFOs family, is used in our samples. APFO3 has an alternating structure made of two segments as shown in the figure 5. One segment is of fluorene and the other segment is of thiophene-benzothiazole-thiophene. The absorption spectrum of fluorene mainly lies in the ultraviolet part and blue part of the visible spectrum [9]. So it is necessary to extend the absorption spectrum of fluorene to infrared part and the green part of the visible spectrum, in order to absorb maximum solar light. For this purpose, a segment of thiophene-benzothiazole-thiophene is attached to the fluorene segment, where thiophene acts as a donor and benzothiazole acts as an acceptor. This donor-acceptor-donor (DAD) configuration causes the charge transfer within the polymer and makes the separation between HOMO and LUMO smaller [10]. Therefore the band gap of APFO3 is decreased and absorption spectrum of APFO3 is extended to infrared and green part of the visible

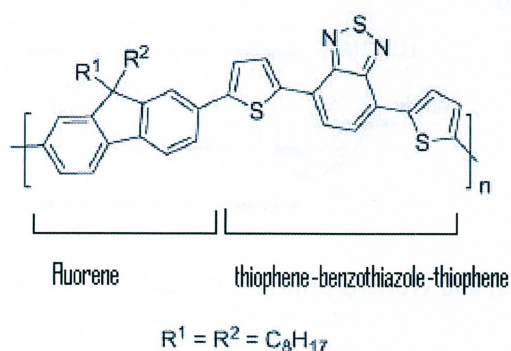spectrum. The HOMO and LUMO values of APFO3 are -5.80eV and -3.41eV respectively [11].

Figure 5. Chemical structure of APFO3 [11].

2.5. PCBM

When light is absorbed by APFO3, the electrons are excited from HOMO to LUMO of APFO3 and leave behind holes in the HOMO of APFO3. These holes in HOMO still have strong Coulombic interaction with electrons in LUMO and it becomes difficult to separate them into free charge carriers. Extraction of free charges is thus not sufficient in APFO3. To increase the yield of free charges, an acceptor molecule is needed that has LUMO value lower than APFO3 LUMO value [9]. The difference $(LUMO_{donor}$-$LUMO_{acceptor})$ also called driving force, helps to transfer the electrons from $LUMO_{donor}$ to $LUMO_{acceptor}$. When electrons are transferred to $LUMO_{acceptor}$, they have comparatively lesser Coulombic interaction with holes in $HOMO_{donor}$ and it becomes easier to separate them into free charge carriers.

Different types of fullerenes are used as acceptors. The most commonly used fullerene for APFO3 is [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM). The chemical structure of PCBM is shown in figure 6a. APFO3 and PCBM are blended together to form bulk heterojunction. The HOMO and LUMO values of PCBM are -6.6eV and -4.1eV respectively [12]. So the driving force for APFO3:PCBM is 0.69eV which helps in efficient charge transfer from APFO3 to PCBM as shown in figure 6b. The charge transfer efficiency for APFO3:PCBM blends, with PCBM concentration ranging from 20% to 50%, has been reported to be 100% [13]. The maximum power conversion efficiency for APFO3:PCBM blended solar cells has been reported to be 3.5% [14].
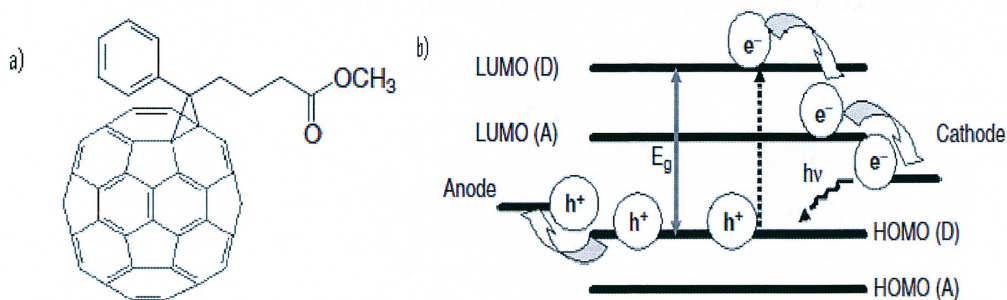
Figure 6. The chemical structure of PCBM a) and Working principle of charge transfer in donor-acceptor polymer solar cell [9].

2.6. Inhomogeneity of Sample

A polymer would have many polymer chains and each chain does not have indefinite length. Each chain has many twists and coils in its structure that gives the polymer it's amorphous nature. If a polymer chain would not have twists, then the π-electrons would be delocalized to the entire polymer chain; but because of twists in the polymer chain, the π-electrons are no longer spread out to the whole polymer chain, and rather are limited to a definite length called conjugation length (chromophores). Also, there are many segments of different conjugation lengths in a polymer. If all segments in a polymer would be of same conjugation length, then the energy of π-electrons delocalized over each segment would also be the same, which would give a sharp absorption and emission spectrum. But all segments of conjugation lengths have different lengths and are also randomly distributed, so that the π-electrons delocalized to each segment have different energies. Therefore a polymer has a broad absorption and emission spectrum. The emission spectrum is red shifted (Stokes shift) as there would be rapid energy transfer between high energy segment and lower energy segment. First, energy is transferred to a lower energy segment, and these lower energy segments then produce the emission spectrum as shown in the figure 7. Thus the random distribution of conjugation length segments in conjugated polymer makes the sample inhomogeneous [15]. Another reason for inhomogeneity of samples is the sample preparation. They are prepared by spin coating over a glass substrate, so the thickness of the sample over the substrate is not uniform. It would be thicker in the middle than at the corners of the glass substrate. In general, all these discussed factors make the sample inhomogeneous.
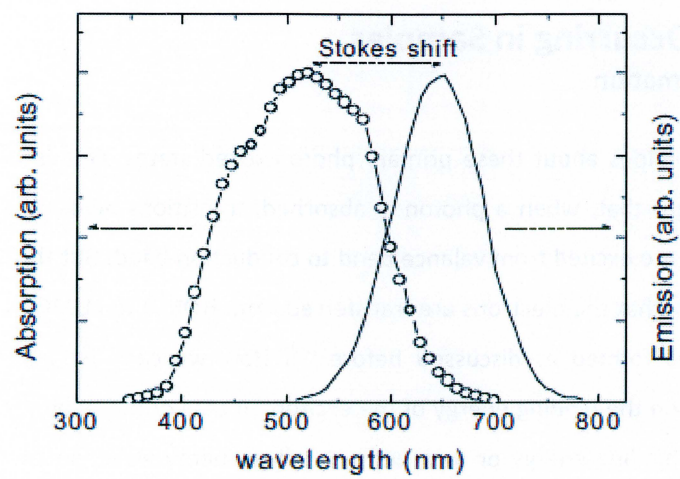
Figure 7. The general absorption and emission spectra of a polymer [7].

3. Processes Occurring in Samples
3.1. Exciton Formation

There are lots of opinions about these primary photo-excited states. One is related to the inorganic semiconductor picture that, when a photon is absorbed, transitions across electronic bandgaps take place, and electrons are excited from valance band to conduction band. But the other picture is related to organic molecules, that the electrons are transferred from HOMO to LUMO of the polymer where π-cloud of electrons is formed as discussed before [16]. How we can distinguish between these two pictures, is based upon the binding energy of the exciton. In case of inorganic semiconductors, excitons may have very low binding energy or may be no binding energy at all, so excited electrons have no Coulombic interaction with the holes in the ground state. But in the case of the molecular picture, the binding energy of excitons is quite high. Many experimental studies show considerably high binding energy of excitons in conjugated polymers [17]. Also, a semiconductor system is considered to be homogeneous, but in polymers, the system is inhomogeneous, as discussed before. Therefore, the molecular picture is more effective in describing the primary photo-excited states and formation of excitons in conjugated polymers.

3.2. Exciton dynamics

When light is incident on the polymer, photons are absorbed and an electron is excited from the ground state S_0 to first excited state S_1 and primary photo-excited states (excitons) are formed. There are a number of processes that can occur after the absorption of light, but first all excited molecules relax down to the lowest energy level of first excited state S_1 (LUMO) of the polymer. This process is called thermal relaxation. After thermal relaxation there are again different processes that can occur in the polymer. One possibility is that molecules will stay in the lowest excited state (LUMO) for some nano-seconds and then decay back to ground state of the polymer (HOMO) by emitting a photon. This process is called fluorescence and the time for which polymer is in excited state is called the life-time of fluorescence. The other possibility is that the system is transferred from the lowest excited singlet state S_1 to triplet excited state. This process is called intersystem crossing, but hydrocarbons with coplanar conformation like conjugated polymers don't suffer intersystem crossing [18].

Thermal Relaxation

S1

Absorption (Excitation): $S_0 \rightarrow S_1$

Thermal relaxation: $S_1 \rightarrow S_1 + heat$

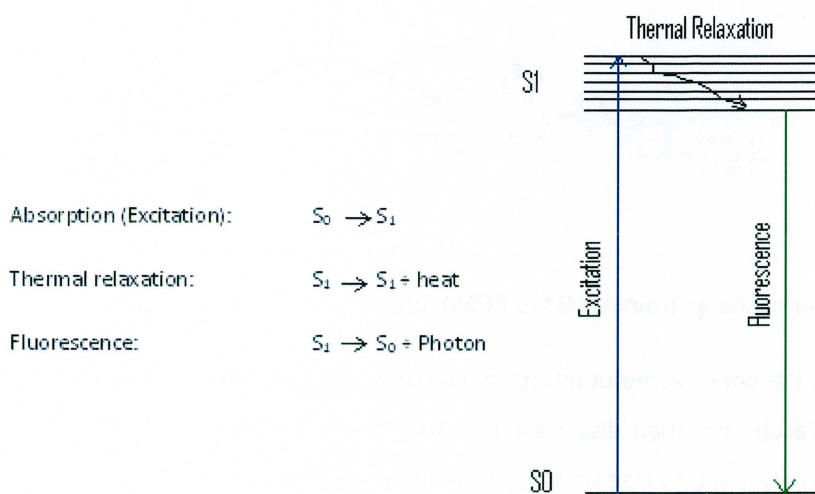Fluorescence: $S_1 \rightarrow S_0 + Photon$

Excitation

Fluorescence

S0

Figure 8: Absorption of light followed by thermal relaxation and then fluorescence.

When an exciton is generated, it has a finite life-time for which it can move. Excitons can travel within the polymer chain and can jump to the neighbouring chains as well, if the chains are closely packed as in a polymer film [19]. This phenomenon is called exciton migration or exciton diffusion and is characterized by exciton diffusion length. Exciton diffusion length is the distance that an exciton can travel before decay. Exciton diffusion length is material dependent, but in most of the polymers it ranges 4-20nm [20].

3.3. Exciton dissociation

Excitons have a characteristic diffusion length and we can find some sites within this length where excitons can be trapped or dissociated into electron-hole pairs. These sites can be a location with significantly lower energy within the polymer, known as a trap, or can be some kind of impurity in the polymer [15]. When excitons are trapped or interact with other molecules, the intensity of fluorescence of the polymer is decreased; this effect is called quenching of fluorescence. In BHJ structures there is a blend of polymer (APFO3) with the acceptor molecule (PCBM) and each generated exciton can find an acceptor molecule within its diffusion length. Therefore charges are transferred to acceptor molecule and the fluorescence of polymer is quenched. It is reported that even at very low concentrations of PCBM (~20%), all fluorescence of APFO3 is quenched and ~100% charges are transferred to PCBM [21].
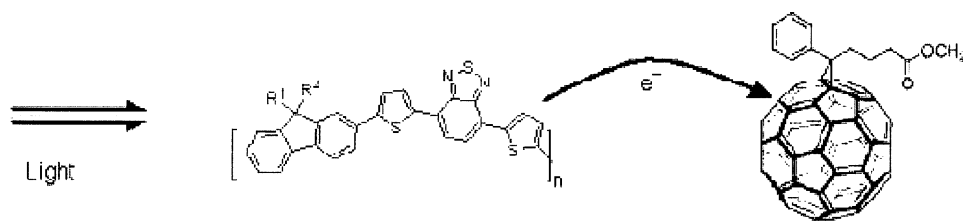
Figure 9: Transfer of charge from APFO3 to PCBM after the absorption of light [22].

When excitons move to the donor-acceptor interface, electrons are transferred from LUMO of donor to LUMO of acceptor molecule and then dissociate into free charge carriers at the interface. But the efficiency of exciton dissociation into free charges at the interface depends upon the nano-morphology which is created when two materials are blended together [23]. However, it is supposed that some intermediate emissive states may be formed, before dissociation into free charge carriers. There are few opinions about the formation of these intermediate emissive states that is discussed afterwards.

3.4. Charge Recombination

When opposite charge carriers recombine with each other, instead of being separated and collected at the electrodes of the polymer solar cells, then that phenomenon is called charge recombination. There are many recombination processes occurring in polymer solar cells that can limit the performance.

The polymer chain is made up of many conjugation lengths. When light (photon) is absorbed, one of these conjugation lengths gets excited. One possibility is that the excited state can decay either radiatively or non-radiatively and the other possibility is that the excited state can diffuse within its diffusion length. When excited state decay radiatively, fluorescence emission is obtained but when excited state diffuses, it forms electron-hole pair. When electron-hole pair is generated, they still have coulombic interaction. If electron-hole pair would not be able to overcome the interaction, they recombine to ground state; this is called electron-hole pair recombination. If electron-hole pair overcomes the interaction, they form free charges.

Once the free charges have been generated, they can recombine either geminately or non-geminately. If free charges remain confined to the same conjugation length, they diffuse and recombine within the conjugation length; this type of recombination is called geminate recombination. Sometimes free charges do not remain confined to the conjugation length from where they were originated. They diffuse to other conjugation length of the polymer and recombine with the free charges produced from

that conjugation length. This type of recombination is called non-geminate recombination. Non-geminate recombination is an intensity dependent process but geminate recombination does not depend upon the intensity of incident light.

4. Conflict about Intermediate Emissive States

4.1. Picture from Transient Absorption technique

Sundström et al. [24] have studied the whole dynamics, right from photo-excitation to recombination of charges in APFO3:PCBM blends. Three different processes have been studied as part of the dynamics. First, after the photo-excitation, all charges are transferred from excited states of the polymer to PCBM molecules, such that all electrons are localized on PCBM and all holes on APFO3. The electronic cloud localized on PCBM has strong Coulombic interaction with holes left on APFO3 and bound electron-hole pairs or bound charge pairs are formed. After the photo-absorption, it is observed that the fluorescence from polymers is quenched, which means all charges have been transferred from APFO3 to PCBM. The time scale for charge transfer from APFO3 to PCBM, after photo-excitation, is ~200fs. This is much faster than the excitation hopping time of ~6ps (the time that excited electrons may take to travel interchain or intrachain in a polymer) which proves that, in BHJ, for each excited polymer segment, there is always a fullerene molecule (PCBM). Thus no unquenched excited state is left in the polymer and all charges are transferred from polymer to PCBM to form bound charge pairs.

The second observed process in APFO3:PCBM blends after the formation of bound charge pairs is generation of free charges. The time scale for the generation of free charges is ~30ps. After generation of free charges the third observed process is recombination of charges. If excitation intensity is low ($<6.6*10^{13}$ Ph/cm^2 per pulse) then intensity independent geminate recombination is the dominant charge recombination process. But if excitation intensity is high ($>1*10^{14}$ Ph/cm^2 per pulse) then intensity dependent non-geminate charge recombination is dominant. Charge recombination processes occur over the same time scale of ~30ns.
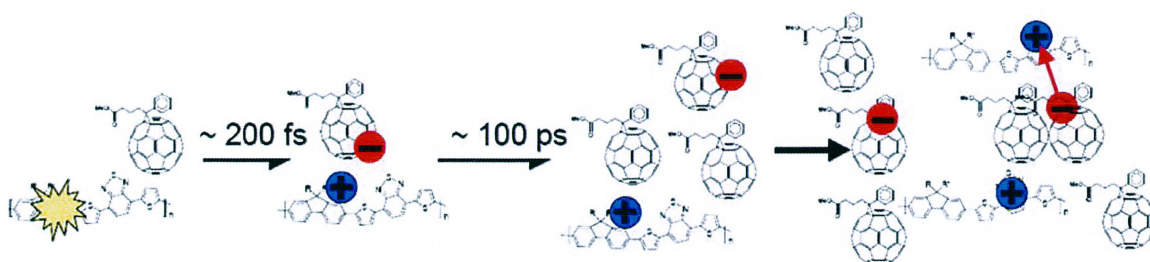

Figure 10: Whole dynamics from Photo-excitation to charge recombination in APFO3:PCBM blends.

In short, the Sundström et al. picture about the whole dynamics in APFO3:PCBM blends is very simple and does not tell us about the formation of intermediate emissive states as shown in the figure 10 as well. But some other researchers believe about the formation of intermediate emissive states and these will be discussed one by one.

4.2. Picture from Theoretical Model

Bredas et al. [25] explain the dissociation of excited states into free charges in two steps. According to this picture, when photons are incident on the system, there will be promotion from the ground state to first excited state and excitons are formed. Excitons diffuse into donor-acceptor interface and dissociate into negative and positive charges. The diffusion of excitons at donor-acceptor interface can be explained in two steps. First when excitons reach the interface, they evolve into charge transfer states D^+/A^- with all electrons localized on acceptor molecules and holes on donor polymer. The charges in these intermediate states stay for some time and then recombine to return to ground state and fluorescence from these intermediate emissive states is obtained. Also, charges from these intermediate emissive states can dissociate into free charges via charge separated states as shown in figure 11. According to Bredas et al. charge separated states are those where positive and negative charges are considered to be free of Coulombic interactions. The Bredas model is theoretical and tells about the formation of intermediate emissive states at donor-acceptor interface before dissociation of excitons into free charges, and also that these intermediate states are emissive. Researchers have measured the life-time of these intermediate emissive states.
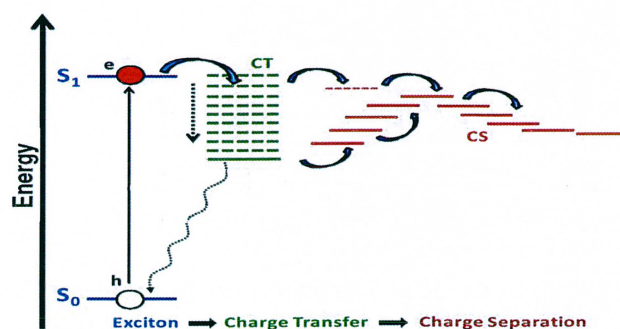

Figure 11: First Excitons dissociate into charge transfer states at donor-acceptor interface and then charge transfer states can either recombine to ground states or can dissociate into charge separated states.

4.3. Picture from Time-resolved Fluorescence technique

Janssen et al. [26] have also investigated the formation of some intermediate emissive states and have measured the life-time of these states as well. According to the Janssen picture, upon photo-excitation, excitons are formed. When these excitons reach the donor-acceptor interface they dissociate and form charge separated states. The charges from charge separated states can then recombine, falling to intermediate emissive states, also called charge transfer states, and then from these intermediate emissive states, recombine radiatively and return to ground state giving fluorescence emission. Janssen et al. also have proposed that when excitons are formed on polymer or PCBM upon photo-excitation, the excitons dissociate and populate these intermediate emissive states directly, rather than dissociating into charge separated states first, as shown in figure 12.

It has also been proposed that these intermediate emissive states have ground state interaction as well, which means these intermediate emissive states can also be populated directly upon photo-excitation as shown in figure 12. But it has been observed that absorption into these intermediate states is very weak. Also, emission from these intermediate states is weak too. The emission from these intermediate states is so weak that it is at best equal to the emission intensity of polymer residues.
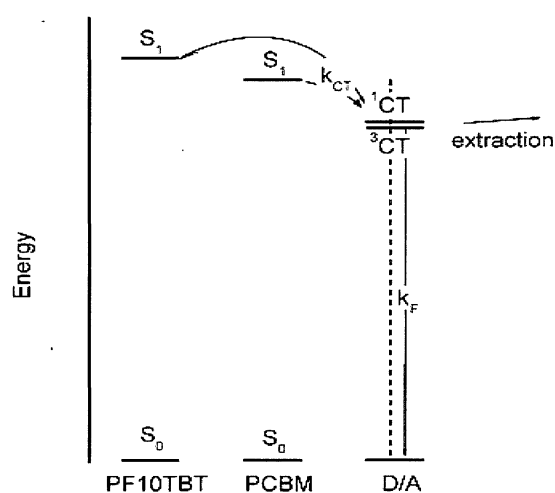

Figure 12: The charge transfer states can be populated from excited states of Polymer or PCBM and also charge transfer states can be populated directly from ground state upon photo-absorption.

4.4. Picture from Electroluminescence technique

Inganäs et al. [27] have also investigated the formation of the intermediate emissive states. Charges (electrons and holes) have been injected into the device. The charges populate the available states in polymer:PCBM blend. It is supposed that the first state that allows the recombination of charges must be the lowest energetic state, and for BHJ structure it is the charge transfer state. It has been supposed that the charge transfer state is interface bound charge pairs that are formed when all electrons are transferred to PCBM and all holes are left on polymer. The electronic clouds on PCBM still has strong Coulombic interaction with holes on the polymer and are called interface bound charge pairs, as shown in figure 13. But the dynamics of charge transfer states have not been measured with electroluminescence technique.
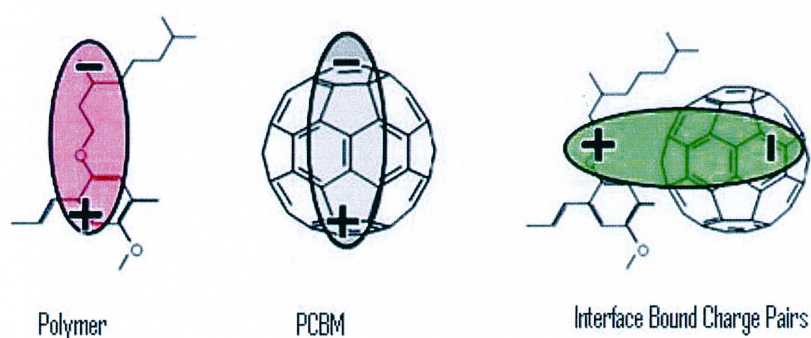

Polymer   PCBM   Interface Bound Charge Pairs

Figure 13: Formation of Interface bound charge pairs at donor-acceptor interface.

4.5. Questions about Intermediate Emissive States

1. The theoretical picture is based upon the formation of charge transfer states and the transient absorption picture is based upon the formation of bound charge pairs. Therefore, is it only terminology difference or are both (charge transfer states and bound charge pairs) different species?

The discussion based upon the pictures from transient absorption technique and time-resolved fluorescence technique raises these questions:

2. Are charge transfer states present in the system (our system is also same) observed under transient absorption picture? As Janssen et al. are working with PF10TBT polymer and Sundström et al. are working with APFO3 polymer.

3. Are some minority species generating charge transfer states in transient absorption picture?

4. Are charge transfer states generate in pure polymer in transient absorption picture? If yes, then are the charge transfer states the lowest excited states of the polymer as shown in figure 5a? Are these states formed because of some traps within the polymer chain or due to some impurity present in the polymer, as shown in figure 5b?

5. Are charge transfer states formed only in APFO3:PCBM blends in transient absorption picture?

6. Are the charge transfer states formed because of recombination of charges in the transient absorption picture?

The discussion based upon the pictures from transient absorption technique and time-resolved fluorescence technique raises this question:

7. Are Inganäs et al. looking at the same charge transfer states whose life-time is ~4ns according to Janssen et al.?
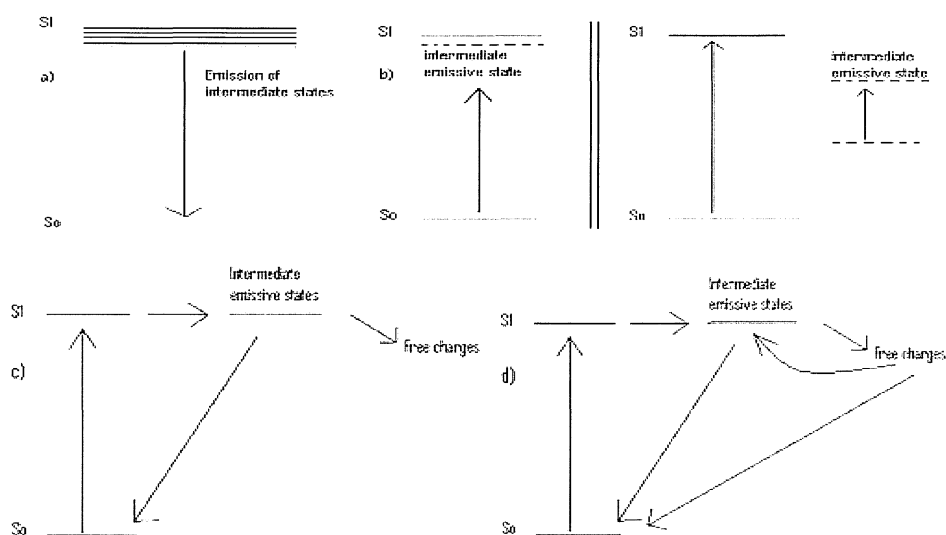

Figure 14: Intermediate emissive states are (a) lowest excited states of polymer (b) some traps or some minority species in polymer (c) formed before charge separated states and (d) formed from the recombination of charge separated states.

We will try to answer these questions, but first we should think about the technique that can be helpful to do that.

5. Time Correlated Single Photon Counting (TCSPC)

If it is supposed that the generated intermediate emissive states are very few, then emission intensity from these intermediate emissive states will be very low. Such a technique is required that should be sensitive enough to detect even very low emission intensity from these intermediate emissive states. Villys et al. have performed Transient absorption technique studies on the whole dynamics, from photo-excitation to recombination of charges in APFO3:PCBM blends. But this technique is not sensitive enough to observe the absorption in minority species, and only the three major processes have been observed. Kristofer et al. has performed electroluminescence technique studies, but with electroluminescence technique the life-times of the intermediate emissive states cannot be measured. So it is not certain that using electroluminescence technique, Kristofer et al. are observing the emission from those same states whose life-time is ~4ns as according to Janssen et al. Thus, such a technique is required that should be sensitive enough to detect even the emission from minor species, and moreover that technique should be a time resolved technique so that the life-time of the minor species can be measured.

Time correlated single photon counting (TCSPC) technique has been built for this purpose. The setup for TCSPC technique is shown in figure 15. It consists of a laser driver that can drive three diode lasers. Turning mirrors are used and are set to such a position that the laser beam from the laser diode is directed to be incident on the sample. Meanwhile, optical density filters are used to reduce the intensity of the incident laser beam. When the beam is incident on the sample, fluorescence from the sample is obtained. Avalanche photo diode (APD) is used to detect the fluorescence emission from the sample. Prior to this, the APD cut-off filters and band pass filters are put in position. Cut-off filters block all light upto a certain wavelength and allow all light above that specific wavelength, while band pass filters allow only a specific wavelength band and block all light below and above that specific wavelength band. APD is connected to a PicoHarp Photon Counter that accumulates the photons and measures the time taken for their arrival, to yield the fluorescence decay. These fluorescence decay traces can be seen on a computer with the help of analysis software "SymphoTime" used for data acquisition and fitting.
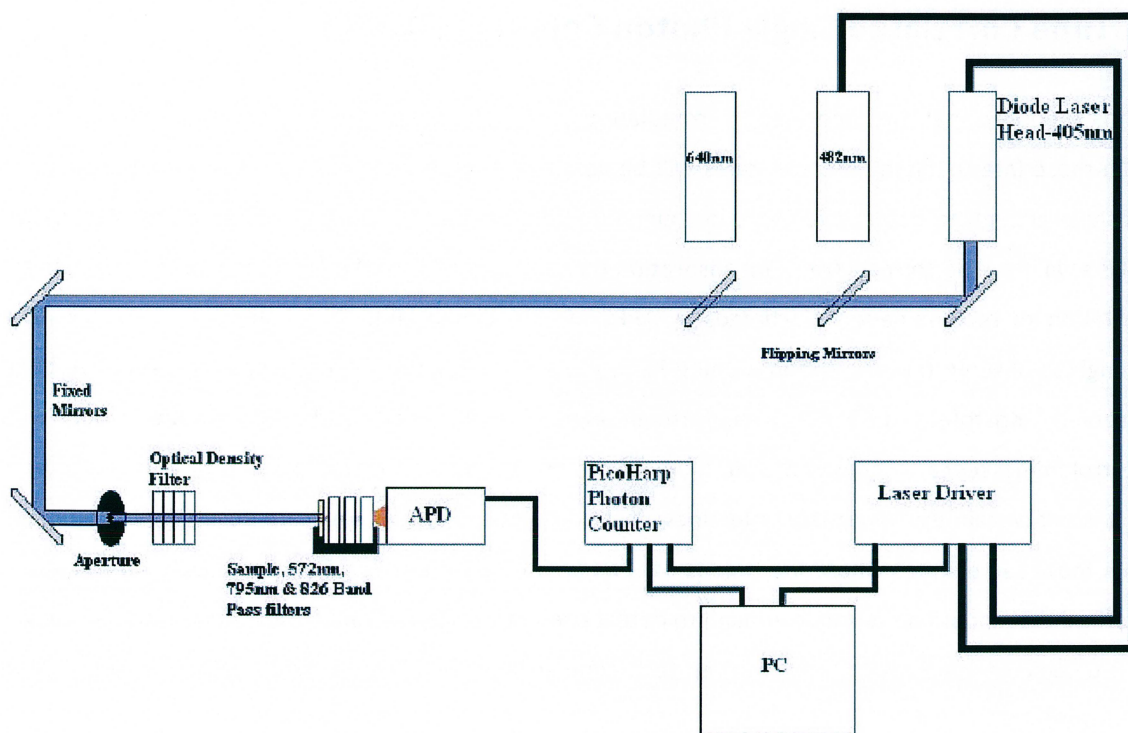
Figure 15: Experimental setup for time correlated single photon counting technique [28].

Thus TCSPC technique has two properties. First it is sensitive enough to detect even a single emitted photon. Secondly it is a time-resolved technique and gives us the appropriate time resolution to measure the fluorescence life-times as well. This means even if the emission of intermediate emissive states is because of some minority species, our technique can possibly detect it. The advantage of time-resolved technique over the transient absorption technique is that the time-resolved technique can resolve the process further. It means that if a process has contribution of many species then transient absorption technique will show the kinetics of major specie only. On the other hand, the time-resolved technique shows the kinetics of all the minor species as well. When we apply fluorescence decay kinetics having the contribution of many species, then we do multiexponential fitting to get the life time of each contributing fluorescence emissive species. Once we know the different life-times, we can assign these life-times to different processes with the help of literature studies. In short TCSPC is quite a good technique to resolve or isolate the contribution from fluorescence of intermediate states and we can measure the life-time of these intermediate emissive states with the help of multiexponential fitting.

6. Results and Discussion

6.1. Absorption and Steady state Fluorescence spectra of APFO3

The absorption spectrum of APFO3 is analysed to find out the wavelength at which APFO3 absorbs maximum energy, so that APFO3 should be excited at those wavelengths to get maximum fluorescence intensity. The absorption spectrum of APFO3 is measured using the "Absorption Spectrometer-Agilent 8453 UV-Visible" apparatus. A brief description of the working of this absorption spectrometer can be found in ref [28]. The absorption spectrum of APFO3 is shown in figure 16a which displays two absorption peaks at 384nm and 540nm. It means absorption by APFO3 is maximum at these two wavelengths so APFO3 should be excited at these two wavelengths to produce maximum fluorescence intensity.
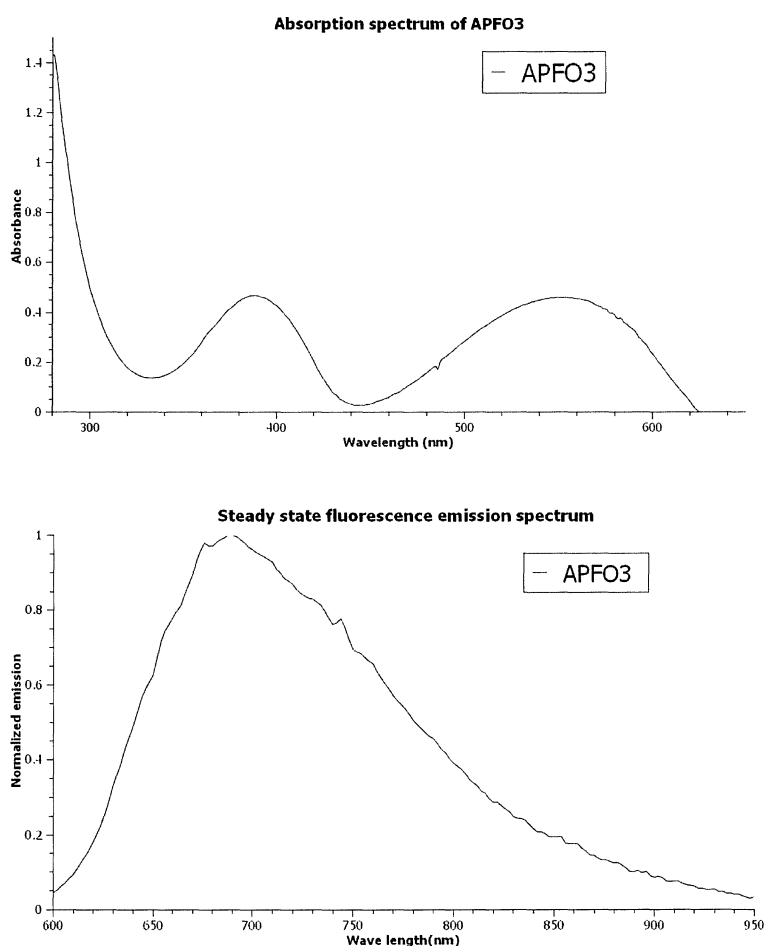

Figure 16: Absorption spectrum of (a) APFO3 and (b) steady state fluorescence spectrum of APFO3.

After measuring the absorption spectrum of APFO3, the steady state fluorescence spectrum of APFO3 is measured. APFO3 is excited using a laser beam of 405nm. The apparatus used to measure this steady state fluorescence spectrum is the "Steady State Spectrometer-SPEX". The basic reading about the working of SPEX can be found in ref [28]. The steady state fluorescence spectrum of APFO3 is shown in figure 16b in which a broad spectrum has an emission maximum at 688nm and a trail of emission lies even in the infrared region.

The absorption and steady state fluorescence spectra of PCBM have not been measured but it is known from literature studies that the absorption maximum of PCBM lies in the ultraviolet region and the emission maximum is at 720nm[26].

6.2. Intensity Independent Processes in Sample

We want to run our experiments in such an intensity range of the laser beam that intensity dependent process shall not occur in the samples. The most common example of intensity dependent processes in polymer solar cells is non-geminate recombination of charges. First the samples are studied under minimum power of laser beam (12μW) and a fluorescence decay trace is obtained. Then samples are studied under maximum power (43μW) of laser beam and again fluorescence decay trace is obtained. If both traces overlap with each other, it means the kinetics remains the same for both minimum and maximum power of laser beam and no intensity dependent process is occurring in the samples even with maximum power of laser beam.

First 4-1 APFO3:PCBM blend is tested for intensity dependent processes. The fluorescence decay traces obtained for minimum and maximum power overlap with each other as shown in figure 17a. The experiment is repeated for 1-1 APFO3:PCBM blend and the result is regenerated again as shown in figure 17b. It means that intensity dependent processes are not occurring in our samples even for maximum intensity of laser beam.

Now we compare our results with literature. We know that intensity dependent processes occur in the samples when excitation intensity is greater than $1*10^{14}$ Ph/cm^2 per pulse and purely intensity independent processes occur if excitation intensity is lower than $6*10^{13}$ Ph/cm^2 per pulse [24]. Now we calculate the excitation intensity in our case:

The minimum power of laser beam = 12μW

The maximum power of laser beam = 43μW

Radius of laser beam = 0.1cm

Repetition rate of laser pulse = 10 MHz

Number of Photons/cm^2 per pulse = $\frac{\lambda t}{hc(\pi r^2)}$

For minimum intensity, Number of Photons/cm^2 per pulse is $7.7*10^7$.

For maximum intensity, Number of Photons/cm^2 per pulse is $2.8*10^8$.

It is clear from calculations as well that the excitation intensity is within such a range that there is no intensity dependent process occurring in the samples. Thus non-geminate recombination of charges is not occurring in our samples.
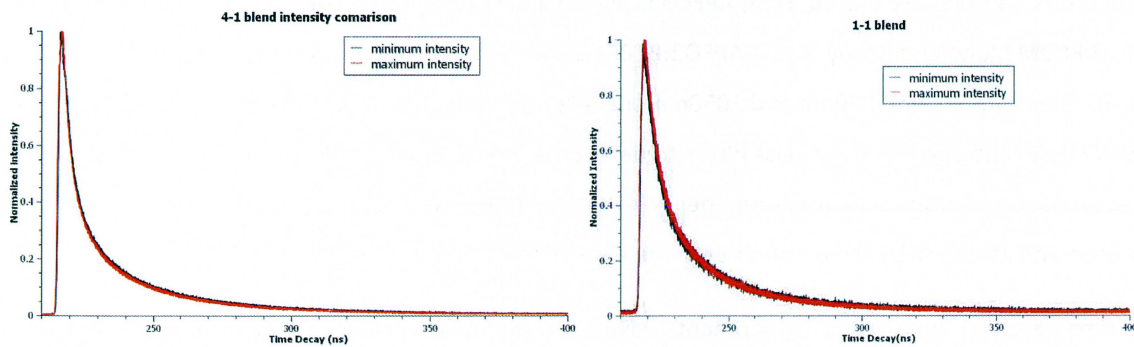
Figure 17: Fluorescence decay traces for minimum and maximum power of laser beam overlap with each other for (a) 4-1 APFO3:PCBM blend and (b) 1-1 APFO3:PCBM blend.

6.3.   Time-Resolved Fluorescence Experiments

The APFO3 used in our experiments has been prepared according to ref [29] with molecular weight M_w=11800. The APFO3:PCBM blends are prepared in chloroform solution with APFO3:PCBM ratios 4-1 and 1-1 by weight. The thin films are spin coated on a glass substrate. Thickness of film is ~90-140nm [30]. The thin films are covered with a glass sheet to protect from exposure to oxygen.

Time-Resolved fluorescence experiments have been performed using time correlated single photon counting technique. A Diode laser with 30ps pulse duration and 10MHz repetition rate has been used. The samples have been excited with 405nm wavelength and the kinetics has been observed at different wavelengths using band-pass filters. The fluorescence decay traces have begun to be observed using 826nm band-pass filter. The one purpose to start observing fluorescence decay traces from 826nm is to block the emission from APFO3 and PCBM. Secondly, according to Janssen et al., the maximum of emission from charge transfer states lies at 820nm. Three different samples, neat polymer APFO3, 4-1 APFO3:PCBM blend and 1-1 APFO3:PCBM blend have been studied. After that, a 572nm cut-off filter is used to block the incident wave length. Further, if this filter is giving its own emission when 405nm is incident on it, then to separate those emissions of the 572nm filter, another cut-off filter, for 795nm, is used. The combination of these two filters is found to be good to block incident light as well as to block emission from first filter (572nm). Samples are placed just before these filters. Now readings are taken using 826nm, 900nm, 950nm and 1050nm band-pass filters one by one, placing them just ahead of the APD. In the first step, 826nm filter is placed succeeding the 572nm+795nm filter, and just in front of these filters, samples are placed. First, APFO3 is placed and readings are taken, then it is replaced by 4-1 APFO3:PCBM blend and finally by 1-1 APFO3:PCBM blend. Same procedure has been repeated replacing 826nm filter with 900nm, 950nm and 1050nm one after the other. Avalanche photo diode (APD) is used immediately following the band-pass filters to detect the emitted photos. PicoHarp is connected to APD to accumulate photons and measure their respective times, so that fluorescence decay traces are obtained and can be seen on computer with the help of analysis software "SymphoTime".

The time-resolved fluorescence experiments have been performed and first fluorescence decay traces have been observed at 826nm for all samples. All traces are normalized and are drawn together as shown in figure 18a. It can be observed from figure 18a that fluorescence decay for APFO3 is faster than for APFO3:PCBM blends. It can be explained that in case of pure Polymer (APFO3), when laser beam is incident on the sample, the electrons are excited from ground state to excited state of the polymer and excitons are formed. These excitons stay there for some time and then decay back to ground state, so fluorescence from the polymer is obtained. But in case of APFO3:PCBM blends, having PCBM concentration ranging from 20% to 50%, the charges are transferred from polymer to PCBM and the fluorescence of polymers is quenched. Thus, relatively delayed decay traces are obtained for APFO3:PCBM blends. The same experiments have been repeated and fluorescence decay traces have been observed at 900nm, 950nm and 1050nm for all samples. The results were the same again, as shown in figure 18b and figure 18c. The fluorescence decay traces at 1050nm are not shown because

they were very noisy. Therefore it can be suggested that the delayed fluorescence decay from APFO3:PCBM blends are not originating from the polymer.
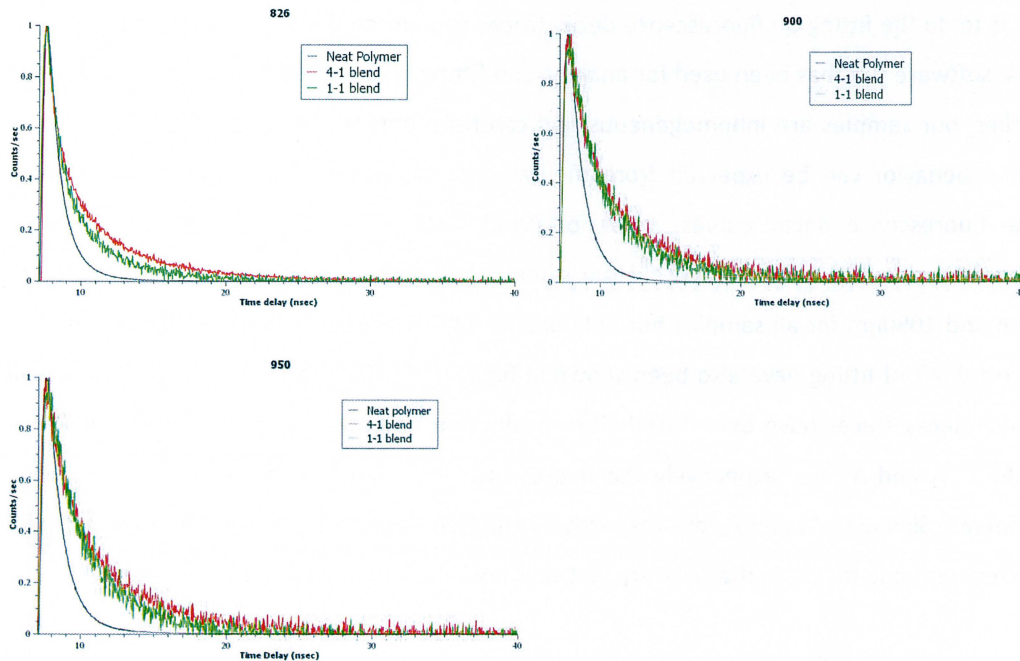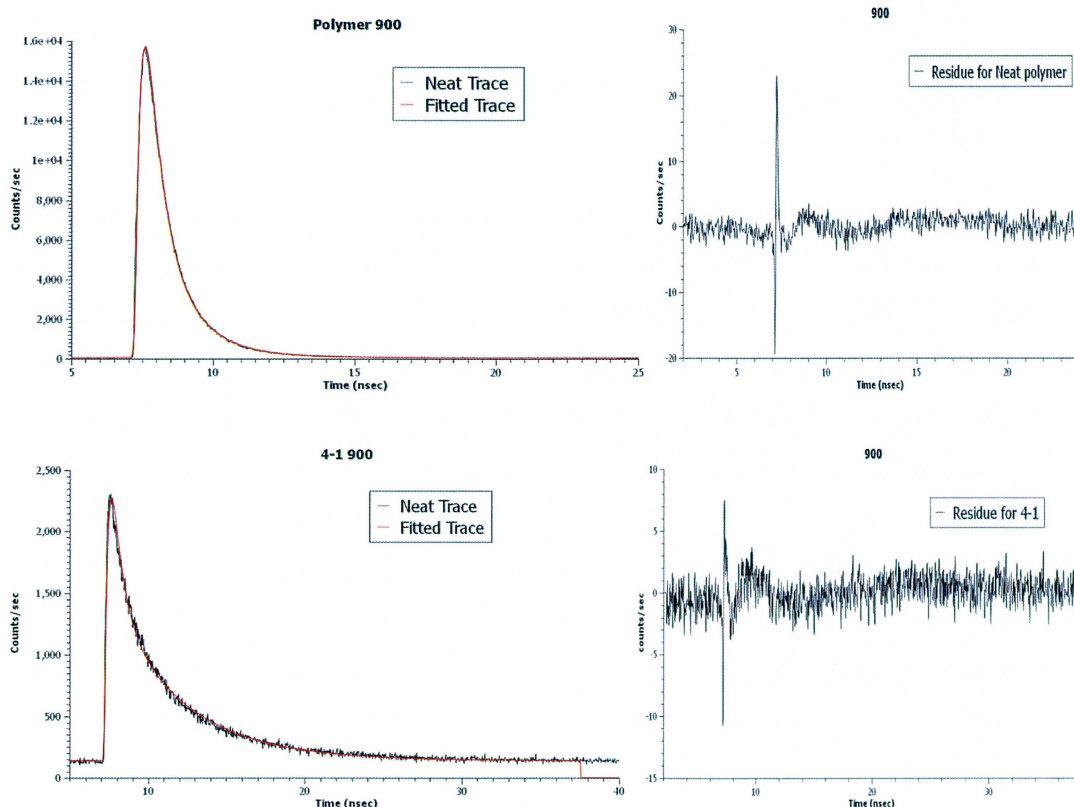

Figure 18: Fluorescence decay traces for APFO3, 4-1 APFO3:PCBM blend and 1-1 APFO3:PCBM blend at (a) 826nm, (b) 900nm and (c) 950nm.

It can also be observed from figure 18a, 18b and 18c that fluorescence decay traces for all samples first overlap with each other for some portions. This means, for that small part of fluorescence decay traces, the kinetics are the same for polymer and APFO3:PCBM blends. But for the rest of the longer part, the fluorescence decay traces do not overlap with each other for all samples, meaning that for those parts, the kinetics are different for polymer and APFO3:PCBM blends. Thus fluorescence decay traces for each sample can be divided into two parts. The initial shorter part for which fluorescence decay traces for all samples overlap with each other can be called a relative shorter component and the remaining longer part for which fluorescence decay traces do not overlap, can be called the relative longer component. As the fluorescence decay traces overlap for relative shorter components for all samples, the kinetics in all samples for this part of the fluorescence decay are the same and can be suggested that this part is from the polymer, even in APFO3:PCBM blends. But for the relative longer component, fluorescence decay traces do not overlap for all samples, implying that the kinetics are different, and it can be suggested that in case of pure polymers, the relatively longer component is due to fluorescence of the polymer

alone, and in case of APFO3:PCBM blends, it is fluorescence from APFO3:PCBM blends rather than from the polymer.

The next step is to do the fitting on fluorescence decay traces so that the fluorescence life-times can be measured. The software that has been used for analysis and fitting is called "SymphoTime". As we have described earlier, our samples are inhomogeneous and can have different fluorescence species. Thus non-exponential behavior can be expected from the samples. When we did the fitting with single exponent, the fluorescence decay curves were not fitted well. Upon doing the fitting with two exponents, the fitting was quite good. We did the same to all fluorescence decay traces at 826nm, 900nm, 950nm and 1050nm for all samples but only one at 900nm has been shown in figure 19a, 19c and 19e. The residuals of fitting have also been shown in figure 19b, 19d and 19f to establish how well the fluorescence decay traces have been fitted. The results that have been obtained after fitting are shown in table 1. T_1 and A_1 are respectively the fluorescence life-times and amplitudes of relatively longer components. Similarly, T_2 and A_2 are respectively the fluorescence life-times and amplitudes of relatively shorter components . X^2 is the quantity that tells how well is the fitting has been done.
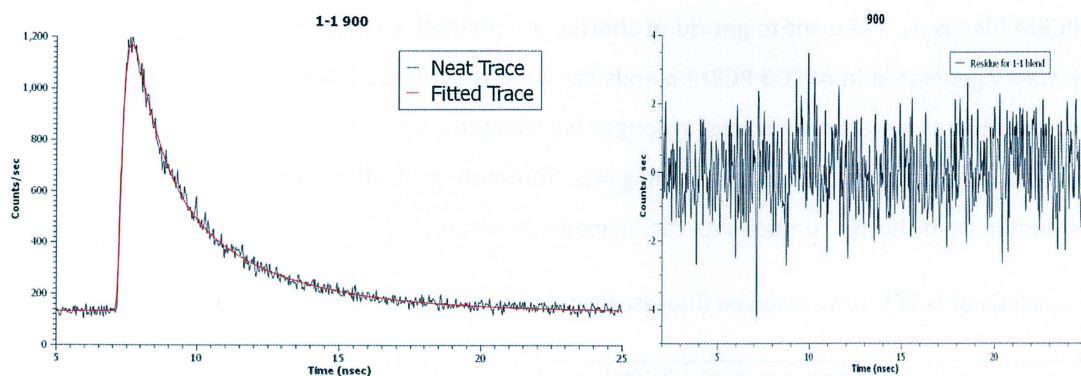
Figure 19: Fitted fluorescence decay traces at 900nm for (a) APFO3, (c) 4-1 APFO3:PCBM blend and (e) 1-1 APFO3:PCBM blend and their respective residual are shown in (b), (d), and (f).

First we look at fluorescence life-times of relative longer components T_1. For polymer (APFO3) it is ~1.5ns and this time period can be assigned to the fluorescence emission of the polymer, which is obtained when, excitons in excited states of polymer decay back to ground state. For 4-1 APFO3:PCBM blend, fluorescence life-time is ~4.45ns, which is delayed compare to pure polymer, hence again, we can justify our statement that charges have been transferred from polymer to PCBM and fluorescence of polymer has been quenched. Thus, emission is not from polymer. For 1-1 APFO3:PCBM blend, the fluorescence life-time is ~3.95ns which is again delayed than pure polymer. The delayed life-times in both APFO3:PCBM blends are the result of some intermediate emissive states that exist in APFO3:PCBM blends only. The variation in life-time measurements even for the same sample, when observed at different wavelengths, is because of inhomogeneity of samples. According to Janssen et al. the life-time of the relatively longer component is ~1.17ns for polymer (PF10TBT) and is ~4ns for PF10TBT:PCBM blends. So our results are quite similar and the slight variations are because of working on different yet quite similar polymers.

Now we look at fluorescence life-time of relatively shorter components. For polymer, it is ~0.68ns and for APFO3:PCBM blends it is ~0.72ns. This means fluorescence life-times for shorter components are almost equal for polymer and APFO3:PCBM blends, which justifies our statement that the source of this shorter component is the same for both polymer and APFO3:PCBM blends. Therefore the shorter component is the effect of emission from some unknown part of the polymer even in APFO3:PCBM blends, and can be called as polymer residual emission. Now if we look at the amplitude of shorter component A_2 it can be observed that even at longer wavelengths, the emission intensity of polymer residual A_2 is often equal to emission intensity from intermediate emissive states generated in

APFO3:PCBM blends A_1. We want to get rid of shorter components so that emission from intermediate emissive states generated in APFO3:PCBM blends can be observed individually. If we look carefully by observing the fluorescence decay traces at longer wavelengths, we can see a trend in A_2, which the contribution of shorter components is becoming less. Therefore on further increasing the wavelengths, the contribution from shorter components can be made minimum.

Table 1: Analysis of TCSPC Time resolved fluorescence decay traces of APFO3 and its blend with PCBM.

Sample	Filtered at (nm)	T_1 (ns)	A_1	T_2 (ns)	A_2	x^2
Polymer (APFO3)	826	1.55	0.21	0.69	0.79	12.74
4-1 APFO3:PCBM blend	826	4.08	0.33	0.40	0.67	3.71
1-1 APFO3:PCBM blend	826	3.21	0.27	0.60	0.73	1.04
Polymer (APFO3)	900	1.33	0.32	0.52	0.68	4.14
4-1 APFO3:PCBM blend	900	4.51	0.43	0.64	0.57	1.72
1-1 APFO3:PCBM blend	900	3.99	0.43	1.05	0.57	1.04
Polymer (APFO3)	950	1.94	0.39	0.89	0.61	3.96
4-1 APFO3:PCBM blend	950	4.51	0.52	0.77	0.48	1.10
1-1 APFO3:PCBM blend	950	5.00	0.43	1.59	0.57	1.01
Polymer (APFO3)	1050	1.20	0.48	0.62	0.52	2.59
4-1 APFO3:PCBM blend	1050	4.72	0.54	1.09	0.46	0.86
1-1 APFO3:PCBM blend	1050	3.63	0.53	2.39	0.47	0.92

One thing is clear from the whole of the above discussion: that the delayed emission from APFO3:PCBM blends are because of some intermediate emissive states generated only in APFO3:PCBM blends. The fluorescence life time of these intermediate emissive states for 4-1 APFO3:PCBM blend is ~4.45ns and for 1-1 APFO3:PCBM blend is ~3.95ns. Now if we compare the life-times of some other processes, the situation would become clearer. We have inferred that the time-scale for charge transfer from polymer to PCBM is ~200fs. The time-scale for separation of charges into free charge carriers is ~30ps and the time-scale for geminate recombination of charges is ~30ns. If intermediate emissive states would form from the recombination of charges, then fluorescence life-time of these intermediate emissive states would be greater than the time-scale for geminate recombination of charges, while using TCSPC technique. But fluorescence life-time of these intermediate emissive states is actually less than the time-

scale for geminate charge recombination. Therefore, using TCSPC technique, it can be said that the intermediate states are not formed by the recombination of charges.

6.4. Degradation in Samples

We want to study the stability of our samples. First we were integrating the samples for 5 minutes, then we increased the integration time to 10 hours and the intensity signals that were observed are shown in figure 20.
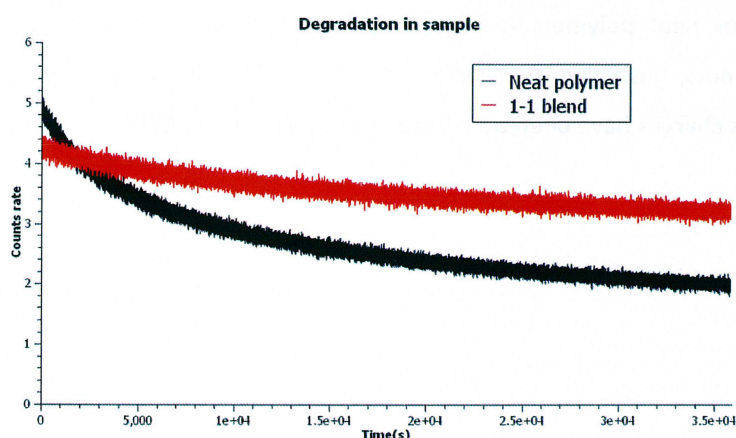

Figure 20: Stability/Degradation in samples.

The first time we illuminated the neat polymer for 10hours, which is shown as the black curve in the figure 20. The intensity signal is degrading for all of the time period. In the initial hours, degradation in samples is high, but decreases with time. During the final hours, intensity curve of the signal is almost smooth. Later, 1-1 APFO3:PCBM blend was illuminated for 10 hours and the intensity signal is shown in the figure 20. For 1-1 APFO3:PCBM blend, again degradation is high initially, and quite lower for subsequent hours, and the curve almost becomes smooth in the end. The degradation in intensity signals can be because of photo bleaching (PB). There are lots of fluorophores (in our case chromophores) in the sample. These fluorophores go to excited states when illuminated with light and gives fluorescence on decaying back to ground state. When these fluorophores are excited for a long time, they may be damaged and may lose their fluorescing property. This phenomenon is called photo bleaching. It can also be possible that when samples are illuminated for long durations, the chemical structures of molecules are also changed. Old bonds may break down and new bonds may be formed.

That would mean some new species have been generated and these new species may have their own spectral properties.

It can be suggested that degradation in samples can be either because of photo bleaching, or because of formation of new molecules. For long advances in time, the intensity signal curves become smooth, which means the samples have been damaged completely or have changed chemically. The visual inspection of the samples after 10 hours showed a transparent spot at the point where we had been illuminating the samples, which justified that the sample had been truly damaged. It can also be observed that the intensity signal for neat polymers is higher than the intensity signal for 1-1 APFO3:PCBM blend in the initial hours, justifying our statement that in APFO3:PCBM blends, fluorescence of polymer is quenched as charges have been transferred from polymer to PCBM.

7. Conclusion/interpretation of data

We had raised some questions about intermediate emissive states and after performing different experiments, we have gotten some results. In the light of these results, we answered some questions. First we were interested in observing time-resolved fluorescence decay traces in such an intensity range of the incident laser beam that no intensity dependent process occurs in the samples, since under solar illumination, only intensity independent processes would occur in polymer solar cells. We performed experiments on samples and showed from their kinetics that no intensity dependent processes have been occurring in the samples. Thus non-geminate recombination of charges, which is an intensity dependent process, is not occurring in the samples under study.

1. To distinguish between the charge transfer state from theoretical picture and bound charge pair from transient absorption picture, we need faster time resolution.

2. Inganäs et al. observed some delay traces in APFO3:PCBM blends, which is an indication that charge transfer states are present in Sundström et al. system (our samples are also same).

3. Some minority species in transient absorption picture are generating charge transfer states and TCSPC technique based on time-resolved fluorescence is good enough to relove the contribution of minority species as well.

4. We performed time-resolved fluorescence experiments and got fluorescence decay traces, for all samples, at different wavelengths. We observed delayed fluorescence decay traces in APFO3:PCBM blends compared to pure polymer, and we said that in APFO3:PCBM blends, charges are transferred from polymer to PCBM. Thus, fluorescence of polymer is quenched and delayed fluorescence in APFO3:PCBM blends are from some intermediate emissive states (charge transfer state) generated in APFO3:PCBM blends only.

5. The charge transfer states are generating in APFO3:PCBM blends, but it is still question that either some of the bound charge pairs of transient absorption picture are generating these states or some minority species at the interface are generating these states.

6. we did the fitting on fluorescence decay traces to measure the life-times of these intermediate emissive states, and they were ~4.45ns for 4-1 APFO3:PCBM blend and ~3.95ns for 1-1 APFO3:PCBM blend. The life-time of these intermediate states is smaller than the time-scale for

geminate recombination of charges, therefore the intermediate emissive states (charge transfer states), we are observing using TCSPC technique, are not being formed from the recombination of charges.

7. Some states may form from the recombination of charges, but using the TCSPC technique, we are not looking for states that are arising from the recombination of charges.

Acknowledgement

I would like to thank my supervisor, Professor Arkady Yarstev, for giving me opportunity to work for such a great environment and for your never ending optimism.

I would like to thank Tomas Österman, a Ph.D. student, for sharing his intelligence and profound knowledge with several scientific fields.

Many thanks go to the members of the Chemical Physics division for their utter willingness to answer any question or provide help in any way.

I would like to thank my Parents and my friends for their great support. At the end, I would like to thank to Allah Almighty to give me power and opportunity to work with good and intelligent people.

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