Charge carrier generation in a polymer by using n-type doping for the improvement of electrical properties

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ABSTRACT

In this paper, the charge carrier generation in polymer blends by chemical doping has studied. In these studies, we employed n-type dopant molecule decamethylcobaltocene (DMC) which exhibit very strong electron donating nature. We have demonstrated that such type of doping favours the formation of charge transfer complex (CTC) and reduce the recombination probability. We have confirmed the CTC formation form the absorption spectroscopy. Further we have used transient photoluminescence spectroscopy to reveal the reduced initial recombination of charge transfer exciton. We interpret our results based on a reduced formation of emissive charge transfer excitons in doped blends, induced by state filling of immobile tail states in the polymer HOMO. Copyright © 2016 VBRI Press.

Introduction

It has been recently explored that the electrical properties of solution process able semiconductors can be tailored by doping with n-type or p-type dopants [**1-4**]. Doping of conjugate polymer may increase the free charge carriers and hence the conductivity by the orders of magnitude. There are several reports to show an increase in electrical conductivity or increase in free charge carriers whereas the effect of doping on the optical excitations is less investigated. In this report we show the effect if doping on the optical excitations since the optical excitation also play the similar role in the functioning of optoelectronic devices such as organic light emitting diodes, organic solar cells. In case of donor acceptor systems, the process of charge photogeneration in is usually described in a series of sequential steps as follows: (i) when the light is absorbed on the polymer blend system, strongly bound interchain excitons of binding energy ~ 0.5 eV are created on the polymer chains [**5, 6**], (ii) These photo generated excitons are diffuses at the donor/acceptor interface, (iii) At the interface, it may be quenched by electron transfer from the polymer to the dopant. Thus an electron transfer (or charge transfer) takes place by dissociating the exciton into an electron on the acceptor side and hole remaining on a polymer chain. This process is throughout influenced by an intermediate state. However electron polaron in the dopant and hole-polaron on the polymer domain are bound with significant Coulomb attraction and their overlapped wave function results the formation of charge transfer (CT) exciton state [**7, 8**].

However these CT states are relatively long lifetime and do not significantly contribute to the photocurrent density in photovoltaic applications. It is obvious that the properties and dynamics of CTs in donor acceptor system are of fundamental importance. The correlation between CT excitons and electronic properties of donor acceptor system has recently been subject of considerable attention for experimental as well as theoretical researchers [**9, 10**]. In this paper, we report on the photogeneration of charge carriers, their mechanism and their use in the betterment of transport parameters of donor acceptor system. The main experimental technique for optical studies that we have used are UV absorption (UV), photoluminescence (PL), which is limited to radiative processes and transient photoluminescence (PL), which is capable to calculate the life time of the charge carriers.

Experimental

In this paper, photo excitation dynamics in pristine and decamethylcobaltocene (DMC) doped poly(9, 9-dioctylfluorene) (PFO) polymer were studied. PFO has been purchased from American dye sources. Chemical structure and energy level diagram of these materials are shown in **Fig. 1**. To achieve effective electron carriers, DMC was added into PFO polymer solution resulting in n-type doping. DMC has been purchased from Sigma Aldrich. The n-type doping is preferable due to the

alignment of LUMO of PFO and HOMO of DMC molecule. This allows a favorable electron transfer from dopant to the polymer.
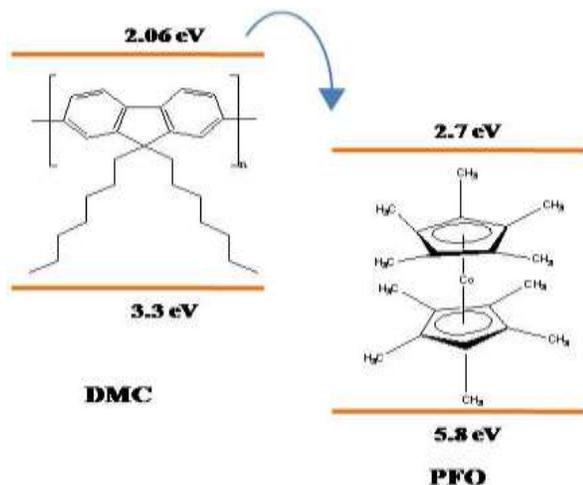

Fig. 1. Chemical structures and HOMO & LUMO positions of materials used for the study.

Thin films of pristine and doped conjugated polymer were prepared in the clean room by spin-coating from filtered millipore filters (0.22 μm) of optimized spin rate. As a first step, the polymer and dopant solutions were separately dissolved in toluene with a concentration of 6 mg/mL and 1 mg/mL respectively. The polymer solution was continuously stirred with magnetic stirrer cum hot plate at 70 °C for 12 h. After being stirred, the solutions were filtered separately. Millipore filters with pore sizes of 0.22 μm were used for filtering solutions, respectively. Blending of the two solutions were done in nitrogen atmosphere. In order to prevent aggregation, we have added 20 μL of Dimethylsulfoxide (DMSO) into the blended solutions. Further, the thin films were prepared by spin-coating using a Karl-Suss spin coater. The solution was spread using a spin speed of 300 rpm for 5 s, then the film was spun with 2500 rpm for 45 s.

Results and discussion

In our optical studies, UV-Vis measurements were carried out by UV-VIS Spectrophotometer (Shimadzu 2401 PC) and NIR measurements were done by UV-Vis-NIR spectrophotometer (Shimadzu 3101 PC). UV-Vis-NIR measurements are 190-3200 nm with resolution of 0.1 nm. Photoluminescence spectra in the visible region have been recorded on high resolution Ocean Optics fiber optics spectrometer Fluorolog Model FL 3-11. To observe the effect of generation of extra electron on the electrical properties of PFO, the electron transport of these samples were studied. For the electron transport as a function of *n*-type doping the electron-only devices were fabricated with the doped PFO layers sandwiched between 100 nm Al. Finally the AFM images were collected using NTMDT solver-pro operated in tapping mode.

CT formation in absorption spectra of doped polymer films

When PFO was doped with different concentrations of dopant DMC, direct electron transfer from polymer to

dopant in the ground state takes place. This will happen due to the preferable alignment of the HOMO of DMC with the LUMO of PFO. Thus as a result of this, background hole density in the polymer without optical excitation. The possible formation of polarons can be seen from absorption study probed by UV-vis NIR spectroscopy in the near-infrared and mid-infrared region. The absorption spectra of pristine PFO and DMC doped PFO with different concentration is shown in **Fig. 2**. The absorption spectra of doped films feature approximately similar to that of pristine film upto 1000 nm but decrease in peak intensities is observed at 383 nm and 428 nm. The small peaks observed in the range of 850-1000 nm in the absorption spectra of PFO may be due to impurities present in the substrate. As the doping level increases, while the lower wavelength transition at 383 nm appears to slight red shifted about 20-30 nm whereas at the higher wavelength transition at 428 nm, no any shift is not observed. This may be observed due to charge transfer complex (CTC) formation. The complex formation can be confirmed from the absorption spectra in the NIR region. The UV spectra of doped PFO thin films in NIR region is shown in the inset of **Fig. 2**. In the near IR region of the absorption of the doped PFO films, two shoulder peak around 1681 nm and 1900 nm are observed (inset of **Fig. 2** shows only the peaked region). These characteristic transitions in the near-infrared and mid-infrared region are attributed due to additionally created polarons. This observation indicates the generation of polaron states in PFO by molecular doping [**11, 12**].
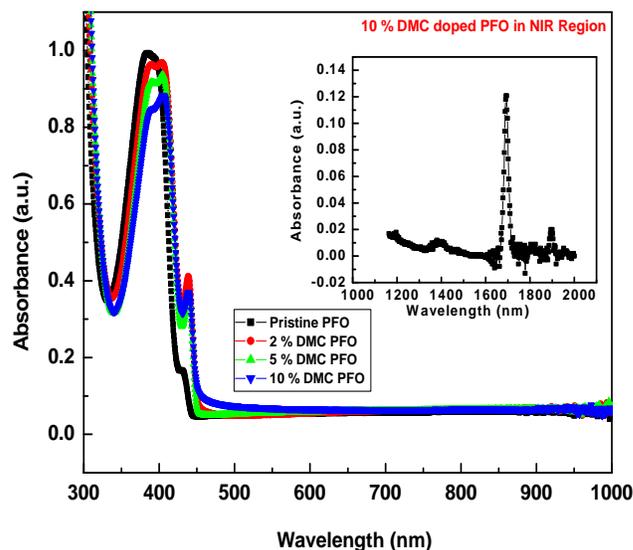

Fig. 2. Absorption spectra of DMC doped PFO films. All absorption spectra are normalized at main peak of PFO. Inset shows the absorption spectra of 10 % DMC doped PFO film in NIR region.

The mechanisms responsible for the polaron formation and consequent quenching have been understood from the schematic as shown in **Fig. 3**. This figure shows the photo induced process of DCM-PFO with their HOMO and LUMO. In the case of DMC doped PF polymer, when, DMC is doped with PF derivative and DMC donor is excited by light, an electron is lifted from the HOMO of DMC to LUMO of DMC. This electron jumps to the adjacent LUMO of PF polymer and CTC will form. Thus finally this doping will become permanent.
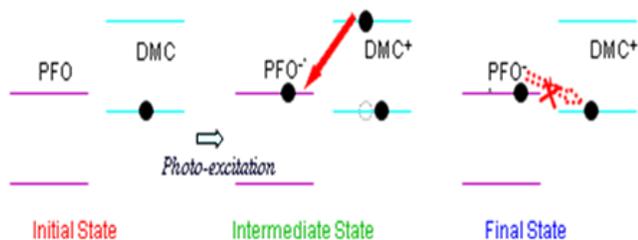
Fig. 3. Mechanism responsible for the polaron formation in polymer: dopant system.

Effect of CT formation on the photoluminescence spectra of doped polymer films

To get more insight into properties of primary excitations; we have used steady-state photoluminescence (PL) spectroscopy. **Fig. 4** shows the PL spectra of pristine and doped polymer samples in different doping ratio. It shows a monotonic reduction of PL intensity in the presence of dopant. Hence, as the doping level in PFO increases, PL intensity continuously decreases. This may be due to the trapping of photo generated charge carriers. As most of the semiconducting systems, photo generated carriers dynamics is mainly caused by the trap states (CTC state). These states occur due to impurities and lie just below the LUMO level. Hence, under the relaxation process, trapped charge carriers may recombine radiatively or non radiatively, producing CT exciton, which is red shifted with respect to the polymer emission. The red shift in the energy of the emissive CT exciton upon the addition of the dopant can be easily seen in **Fig. 4**. PFO has very strong electron donating tendency that assist the formation of a singlet exciton with a strong CT character leading to a red shifted emission [**13, 14**].
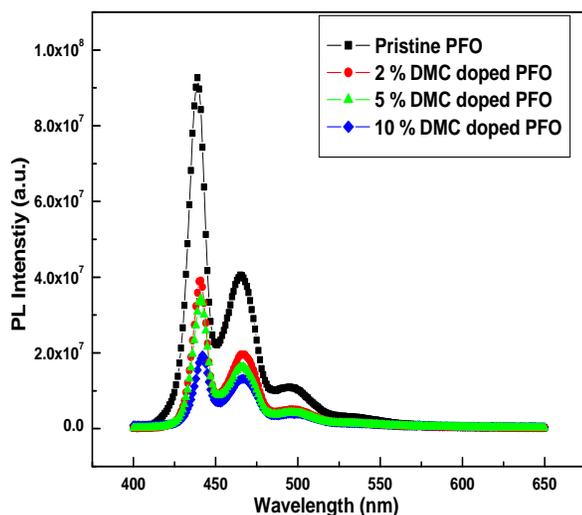

Fig. 4. PL spectra of DMC doped PFO films for different dopant concentration. Excitation wavelength was kept at 380 nm.

Our results give an indication that doping affects the charge generation process, since CT excitons play an important role therein. The observation of intensity as well as the shift in energy of CT exciton upon doping is appealing. But from steady state PL spectra we cannot say anything about doping-related mechanism responsible for

the recombination of CT excitons. The observed decrease in PL intensity may be due to a reduced initial formation of CT excitons or a reduced life time of the emissive CT excitons. Hence for more detailed investigation of CT exciton dynamics, further time-resolved PL experiments on pristine and doped PFO thin films were performed.
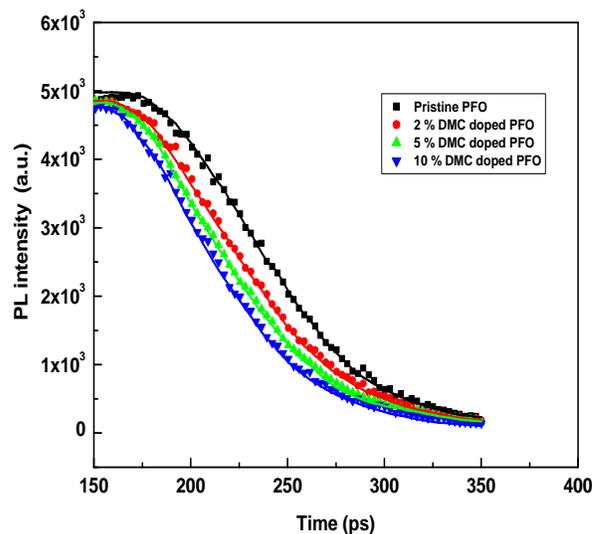

Fig. 5. Transient PL spectra of pristine PFO and DMC doped PFO thin films. A bi exponential decay is observed from frenkel excitons. Theoretical curves are shown by solid lines and fits well with the experimental data.

Table 1. Calculated bi exponential decay constants of pristine and doped PFO films.

Time Decay	Pristine PFO	2 % DMC doped PFO	5 % DMC doped PFO	10 % DMC doped PFO
τ_1	69 ps	44 ps	41 ps	40 ps
τ_2	317 ps	263 ps	233 ps	200 ps

Fast quenching of CT exciton emission in time-resolved PL of doped polymer films

The emitted photoluminescence was detected with nano-LED of wavelength 372 nm with 1 ps pulse width. **Fig. 5** shows the ultrafast PL decay dynamics of the DMC doped PFO sample corresponding to the PL photon energies 3.3 eV. The general characteristics of the decay are the same for both samples.

The ultrafast PL decay has a two-exponential character and this is attributed to the rapid carrier trapping into the interface states, leading to the formation of CT states [**15, 16**]. The slow (ps) component of the ultrafast PL decay can be explained by the relaxation of the trapped carriers to lower energy states. The decay curves show significant decrease in the decay time with doping ratio and these results are tabularized in **Table 1**. To quantify these changes, we have fitted each curve by a two-exponential decay curve as given below:

$$A_1 \exp(-\tau_1 t) + A_2 \exp(-\tau_2 t)$$

The parameters τ_1 and τ_2 stand for lifetime components with amplitudes A_1 and A_2 respectively; A_1 and A_2 are the intensities of each component. The bi-exponential behavior

of the decay curve can be explained by (a) a fast process which might be attributed to relaxation of the carriers into the unoccupied ground state, (b) the slow process can be correlated with radiative recombination from the excited state.

The time resolved PL data can be explained either by assuming that the increased carrier density is induced by the dopant in the polymer domains influences the rate of recombination, changing the non-radiative rate of the CT exciton luminescence; or the carrier density has an influence on the charge separation channel, which lowers the probability for the population of the bound emitting CT exciton and results in separated electrons and holes (polarons). Since, if dopant is added into polymer matrix, some of the electrons are transferred from the HOMO of dopant to the LUMO of Host (n-type doping). Consequently, free charge carriers in the polymer are produced upon doping. These additional free carriers are then captured by empty traps. This additional recombination will lead to the decrease of lifetime of PL with doping.

Improvement of transport properties of PFO after n-type doping

To see the effect of doping on the electrical properties of PFO, single layer device of configuration ITO/PFO: DMC(x %) /Al were fabricated. We used to choose the same concentrations of DMC for the electrical studies as we used for the optical studies. **Fig. 6** shows the J–V characteristics of single layer bipolar devices of doped PFO films. It can be seen from the figure that the current density has increased significantly by the doping of DMC in PFO. Current density was found to vary linearly with voltage in the low voltage range (V < 1 V). This indicates towards an ohmic type conduction mechanism. This mechanism may be attributed to the formation of polaron between PFO and DMC. The polaron formation is already confirmed from the optical absorption of the doped films. The conductivity for all the doped devices has been calculated from the ohmic region of **Fig. 6** and is shown in **Fig. 7** as a function of doping concentration.
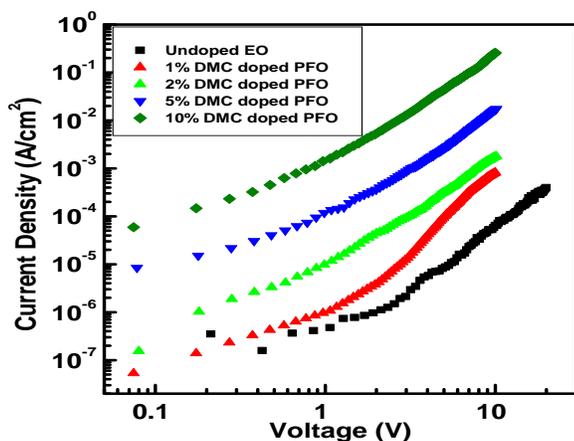

Fig. 6. Current density–voltage characteristics of pristine and DMC doped PFO based electron only devices.

It was recently reported by several authors that the conductivity in doped organic semiconductors is only

increased by filling of trap stated followed by free charge carriers [17].

But in our case we have used such system in which LUMO of the polymer (2.7 eV) is just above to the HOMO of the dopant (3.3 eV). This favors a direct electron transfer from dopant to polymer. The charge transfer from dopant to polymer is already confirmed by the additional absorption peaks in the NIR region (inset of **Fig. 7**). Hence, we have concluded that the increases in conductivity in DMC doped PFO system is due to the direct charge transfer generated from the n type doping of DMC in PFO. Our finding also supports a recent report of Lee *et al.* [**10**]. They proposed that the doping mechanism of organic semiconductors can be influenced by trap states of host organic semiconductors.
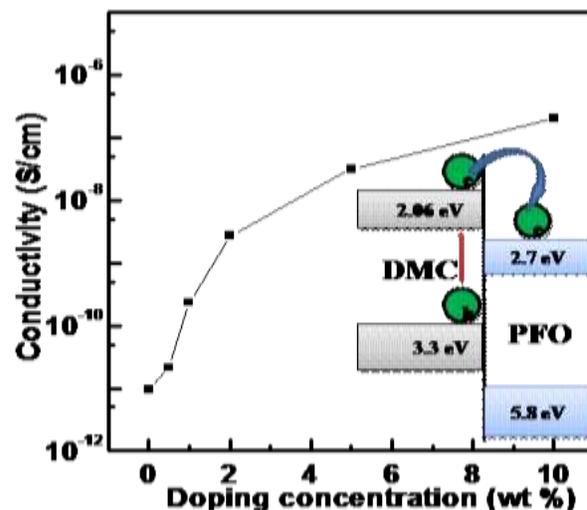

Fig. 7. Calculated conductivity as a function of doping concentrations.
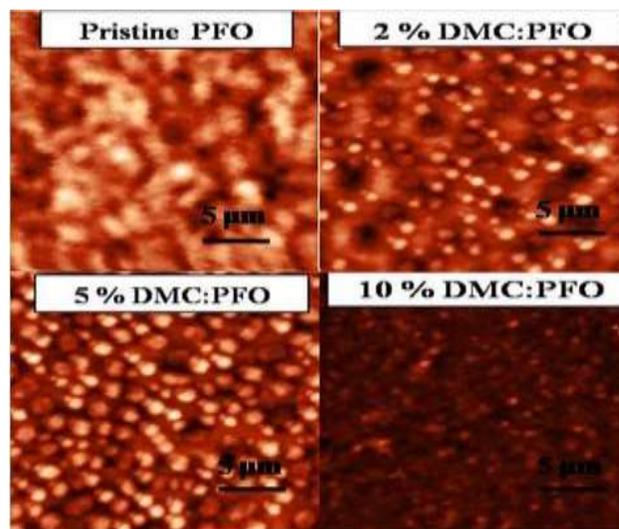

Fig. 8. Topographic image of DMC doped PFO films with dopant concentration.

Morphological investigation of doped conjugated polymer films with AFM and their correlation with transport properties

The AFM experiments give information on changes in film topography due to incorporation of dopant molecules. We studied the morphological properties of pristine PFO and

DMC doped PFO thin films. The morphological images of pristine and DMC doped polymer films are shown in **Fig. 8**. The typical crystalline and fibrillar like structure in PFO films are observed. We attribute this to the low molecular weight of the investigated PFO. However, we have not noticed any pronounced change in film topography after 1 % doping. Further by increasing doping concentrations from 2 % to 10 %, the films show featured morphology as compared to the pristine PFO films with the formation of larger domains. Some studies suggest towards limited charge transport in fibrillar structures due to the reduced interconnectivity of polymer chains and the resistance of defined grain boundaries [**18, 19**]. On the other hand, the nodule-like morphology could provide more pathways for charge transport between polymer chains, as shown in **Fig. 8**. Therefore, the higher mobility is observed in the doped PFO devices.

Conclusion

We have created free charge carriers in PFO polymer by using n-type doping of DMC for the amendment of electronic properties. We performed absorption studied on these samples to detect the polaron formation in absorption spectra of doped polymer films. We demonstrated that doping reduces the interfacial recombination via CT excitons and therefore it results a favorable polaron formation. Further a steady state PL study was performed on pristine and doped polymer samples. We found that photoluminescence intensity with increasing doping ratio. This may be due to trapping of photo generated charge carriers. Subsequently we performed transient PL on these samples to study the decay kinetics in the doped samples. We noticed an ultra-fast initial quenching of CT exciton emission in time-resolved PL. The ultrafast decay component was attributed to an additional recombination of charge carriers. After a complete study of optical properties of these samples we carried out the charge transport studies of these doped samples. For this we prepared a single layer electron only device and we found that the current density increases significantly by the doping of DMC in PFO. Conductivity of PFO was found to be increased from $9.5 \times 10\text{-}12$ S/cm to 2×10^{-7} S/cm due to the filling of traps. These findings were further correlated with the morphological structure of doped conjugated polymer films with AFM.

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