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Charge dynamics in alkanedithiols-additives in P3HT:PCBM bulk heterojunction solar cells

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ABSTRACT

Addition of a small fraction of high boiling point solvent into the host of donor/acceptor blend is one the best approach to control the morphology in order to enhance the power conversion efficiency of organic bulk heterojunction (BHJ) solar cell devices. Herein, we focus on the effect of two thiol-based additives (1,6-hexanedithiol (HDT) and 1,5-pentanedithiol (PDT)) on the charge dynamics of P3HT:PCBM blend system, studied by transient absorption spectroscopy (TAS) and correlated with the solar cell device performance. TAS reveals a more efficient charge generation and polaron formation in the systems with additives as compared to those without (NA systems), at the onset which persists up to few microseconds. The recombination dynamics also exhibits the reduced recombination losses on adding these additives in this system; however, there is marginal change of recombination dynamics in PDT added system with the control. These charge dynamics were validated using the analytical model proposed in our previous work and also correlated with improved device performance ($\eta_{NA} = 0.9\%$, $\eta_{HDT} = 2.7\%$, $\eta_{PDT} = 1.6\%$).

1. INTRODUCTION

Conjugated polymers are being recently investigated and used in designing the bulk hetero-junctions (BHJs) organic solar cells (OSCs) because of their low cost production process, higher light absorption and flexibility[1, 2]. Among numerous donor-acceptor combinations, blends of regioregular poly[3-hexylthiophene] (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C61 (PCBM) are more widely used for high efficiency polymer solar cells during the past few years[3, 4]. To attain higher efficiency in bulk hetero-junctions solar cells, optimum nano-size crystallization of polymers in the blend films is imperative because it leads to better light absorption and improved charge carrier transport properties. Thermal annealing is the broadly used method to enhance the device performance by controlling the physical behavior of the polymer blend[5]. Although annealing improves the performance of solar cells, the active layer is very sensitive to the annealing conditions [6, 7]. For the high volume production, it is imperative to develop a low temperature solution processed technique compatible for mechanically flexible substrates [8-11]. Zhang et al. introduced a solvent mixture method in which two solvents with different boiling points were blended[12]. Salim et al. investigated the effects of self assembles on the model of P3HT:PCBM blend[13]. Here, the authors directly compared the effect of additive's boiling points and solubility on nanoscale phase separation. They found that improvement is not linear with increasing boiling point, but resembles a bell shape[13].

Although it is now generally accepted that P3HT:PCBM based devices fabricated with additives can typically exhibit higher PCEs than those without [14, 15], however systematic studies on the photophysics of these systems are still lacking. To optimize the material properties and morphology of additives-added P3HT:PCBM based devices, it is

imperative to gain a clear understanding of the fundamental photophysical processes governing charge dynamics in system and correlate to the device performance of the solar cell. Investigating the dynamics of the charge generation and recombination in non-annealed (NA) and additives-added P3HT:PCBM films and elucidating the origins of its device performance are the main foci of this work. Herein, we report on a comprehensive study of the carrier dynamics in thin films with different morphology (i.e. non-annealed, HDT and PDT additives added P3HT:PCBM blend) by transient absorption spectroscopy (TAS). Transient optical studies spanning the temporal regimes of charge generation, recombination, transport, and extraction (i.e., over 7 orders of magnitude from 100 fs to 5 μ s) were used in this study. These findings were correlated with the device performance studies of these samples. Femtosecond transient absorption spectroscopy reveals a more pronounced ground state bleach signature in additives-added blend than the non-annealed blend film, suggesting a higher rate of charge generation and polaron formation in the modified system.

2. METHODOLOGY

To prepare the blend solution, P3HT:PCBM (1:0.8) in DCB was stirred overnight at 50 $^{\circ}$ C in a N_2 glovebox. 2% of alkanedithiols by volume was added into this solution which was then stirred for a further two hours before spin-coating. The alkanedithiols chosen for this study were 1,5-pentanedithiol (PDT, $T_b = 216$ $^{\circ}$ C) and 1,6-hexanedithiol (HDT, $T_b = 242$ $^{\circ}$ C) which were bought from Sigma Aldrich. The structures of the both thiol-additives are shown Fig 1. To study the optical properties of these systems, blend films with and without additives were prepared on cleaned glass substrate and dried in glove box. Femtosecond transient absorption spectroscopy (fs-TAS) was performed in a non-degenerate pump-probe configuration. The pump pulses (500nm) were generated from an optical parametric amplifier (OPA) (Light Conversion TOPAS TM) that was pumped by a 1 kHz regenerative amplifier (Coherent LegendTM, centre wavelength: 800 nm; pulse width: 150 fs). The probe beam was a white light continuum generated from a sapphire plate using 800nm femtosecond pulses. Pump induced probe transmittance change (relative differential transmission $\Delta T/T$) was monitored using a monochromator/PMT configuration (for visible probe range). The excitation intensity was ~ 7 μ J cm^{-2} per pulse to minimize higher order effects.



Figure 1. Chemical structures of the solvent additives used (Top) 1,5-pentanedithiol (PDT) and (Bottom) 1,6-hexanedithiol (HDT)

The reference (NA) and additives added P3HT:PCBM solar cell devices were fabricated using well-established steps: (1) Patterned ITO glass was ultra-sonicated in DI-water and in the mixture of acetone: isopropyl alcohol: methanol (1:1:1 by volume) for 15 minutes each and then further cleaned with oxygen plasma; (2) 30 nm PEDOT:PSS hole transporting layer was spin-coated on the ITO and baked in nitrogen filled glove box at 140 $^{\circ}$ C for 10 min; (3) P3HT:PCBM solution in DCB mixed with and without additives was spin-coated to form a 100 nm thick active layer and left for 30 min for drying; (4) A 100 nm aluminium layer was deposited under high vacuum using thermal evaporation. The current-voltage (I - V) characteristics of the devices were measured under illumination with Keithley SMU 2400. The cells were illuminated by an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 100 $mW\cdot cm^{-2}$.

3. RESULTS AND DISCUSSION

3.1 Absorption measurements

Fig. 2 shows the photon absorption spectrum of the NA (thermal free and additive free), and films to which 1,6-hexanedithiol (HDT) and 1,5-pentanedithiol (PDT), (2 vol%) were added to the P3HT:PCBM blend as processing additives. Absorption profile shows the improved photo-absorption in additives-added P3HT:PCBM blend films and are

also more red-shifted than the NA blend film. The absorption of the peaks at 523 nm, 557 nm and 603 nm emerges on addition of additives. The most intense vibronic peak at 557 nm and other at 608 nm refers to the inter-chain interaction in the blend while p-p* transition in P3HT is represented by 523 nm peak [16, 17]. The absorption spectrum shown in the figure designates that addition of additives to the P3HT:PCBM blend indeed has enlarged the amount of well-organized aggregates in the blend film (comparative to the NA film). On the other hand, the spectral profile does not show any significant difference in absorption of both alkanedithiol blends.

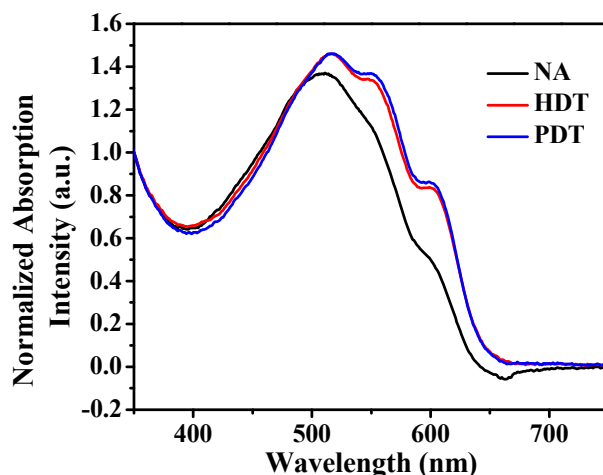
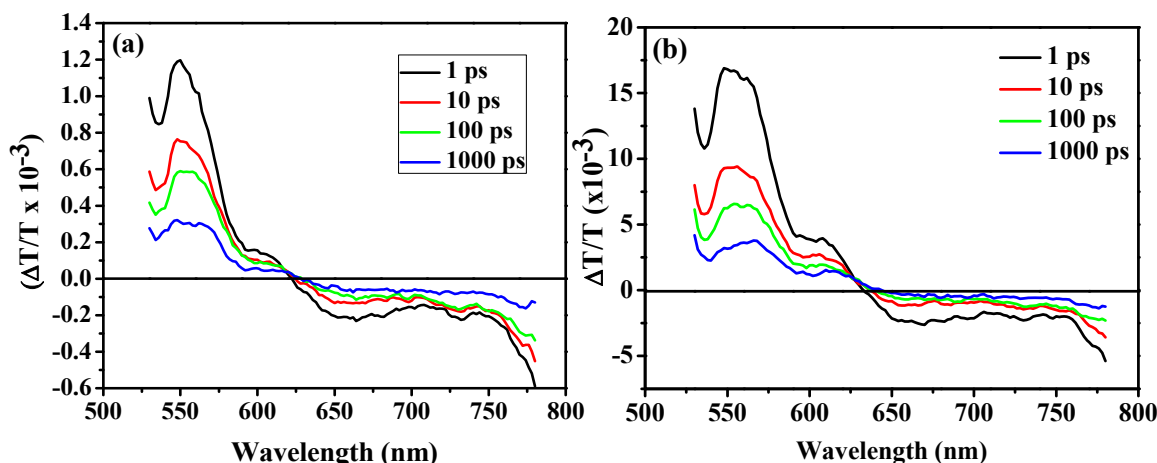


Figure 2: Normalized absorption spectra of the P3HT:PCBM film with and without additives added P3HT:PCBM blend films.

3.2 Exciton Generation and Recombination Dynamics

To probe the exciton generation and recombination dynamics, we performed fs-TAS by exciting the samples with 150 fs pulses centred at 500 nm and record the change in transmission. We monitor the ground state bleaching (GSB) at early delay times to evaluate the relative population of the photogenerated excitons in NA, and additives-added P3HT:PCBM blend films (of thickness 100 ± 5 nm). The GSB, arises by the state-filling of the excited states and represents the population of the photoexcited excitons in the films. Fig. 3 shows the TAS signal from 530 nm to 760 nm at different delay intervals. The GSB of P3HT:PCBM spans from 530 nm to ~ 630 nm. Two peaks can be observed in this region, which corresponds to the 0-0 and 0-1 (in order for increasing energy) vibronic transitions respectively[18]. This is due to the highly crystalline P3HT domains that lead to a strong coupling of lattice phonons with the excitons. Integrating the GSB signal at 1ps from 530nm to 620nm shows that there is an increase of exciton generation by $\sim 64\%$ and $\sim 37\%$ for P3HT: PCBM films on adding HDT and PDT additives respectively.



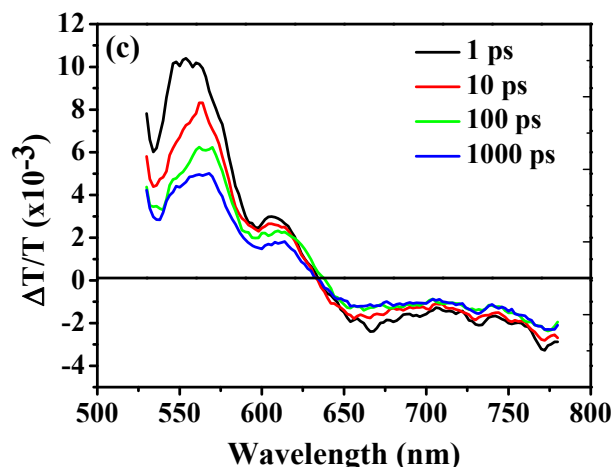


Figure 3. fs-TAS signal spanned from 520nm to 760nm probed at different time delays: (a) Without additive, (b) with HDI (c) PDT added P3HT:PCBM blend films.

The lack of intensity in 0-0 peaks indicates that planarized chain segments are not occupied by holes and this indicates that PCBM disrupts the formation of ordered aggregates. The photogenerated delocalized polarons in P3HT aggregates gives the negative $\Delta T/T$ signal from 630 nm to 775 nm and refers to the photo-induced absorption (PIA). Stimulated emission (SE) region is not observed in all films which indicates the dominance of the polaron signature over that of the excitons[18].

The polaron dynamics were also monitored over longer time scales (1ns-5us) where short-lived photoexcited species have been recombined or dissociated. The dynamics at the 0-0 GSB probed at 560 nm from 1ns to 5μs. Fig 4 shows a plot showing the time dependence of the normalized 0-0 GSB peak decay in NA and HDT, PDT-added P3HT:PCBM blend films. The decay profile shows that 0-0 GSB peak in non-annealed film decay faster while HDT-added film shows the minimum rate of decay. This signifies that photogenerated species in NA film are recombining faster. This recombination can be a combination of trap-assisted recombination (generally considered to be a monomolecular process) and a higher order recombination (attributed to delayed bimolecular recombination under high fluence)[19]. PDT-added film also exhibits the similar decay profile and hence can be assumed similar recombination process but relatively less in magnitude. For the further investigation, the GSB dynamics are fitted as a combination of monomolecular and bimolecular recombination. The details of this model can be found in our previous work [20]. The fitted parameters are shown in Table 1 where k represents the average recombination rate; f corresponds to the contribution from long-lived species and $(\alpha+1)$ is the average recombination order related to the type of recombination and concentration dependence of carrier mobilities. From the fits, the low value of the f indicates that the majority of charges undergo trap-assisted recombination in the NA film P3HT:PCBM system which is in the agreement of the previous reports[21]. The enhancement in the fraction of long lived species in additives added film attribute to the drop of the first order recombination and hence the reduction of trap states in the blend. The minimum value of the average recombination rate in HDT added film shows the existence of the more ordered polymer phases.

Table 1: Fitting parameters for the ns-TAS data

Devices	f	$\alpha+1$	k
NA	0.03±0.00	1.89±0.03	0.03±0.00
HDT	0.06±0.00	1.57±0.03	0.01±0.00
PDT	0.04±0.00	1.82±0.02	0.02±0.00

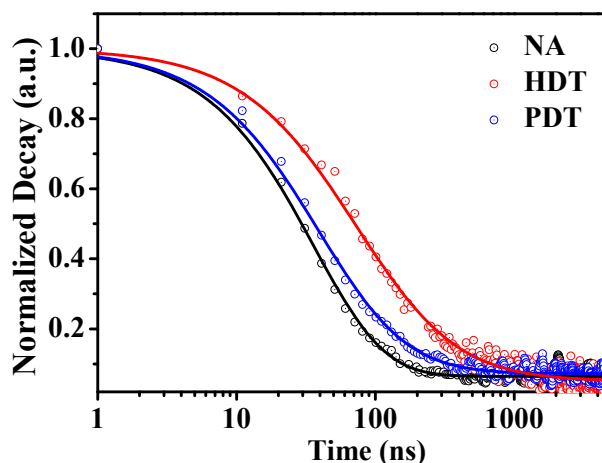


Figure 4: Nanosecond to microsecond transient absorption decay dynamics of GSB 0–0 peak in NA and HDT, PDT added P3HT:PCBM blend films.

3.3 Device performance

Fig. 5 shows the current–voltage (J – V) characteristics of NA, and additives added P3HT:PCBM solar cell devices under illumination of AM 1.5G irradiation at 100 mW cm^{-2} and the summary of the device performance is tabulated in Table 2. The data presented in Fig. 5 are collected from 100 devices. Because of the poor values of short circuit current (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) of the NA devices, it shows the lowest PCE (0.9%). Solar cells prepared by HDT-added P3HT:PCBM blend devices show the better performance ($\eta = 2.7\%$, $J_{sc} = 7.8 \text{ mA cm}^{-2}$, $V_{oc} = 0.54$ and $FF = 0.57$) than PDT-added devices ($\eta = 1.6\%$, $J_{sc} = 7.2 \text{ mA cm}^{-2}$, $V_{oc} = 0.44$ and $FF = 0.50$). The significant enhancement of PCE stems from the improvement in J_{sc} and FF . The improved FF of the devices indicates a low internal resistance in the blend devices. Hence the, improved current density and FF of the devices can be correlated to the lower series (R_s) and higher shunt (R_{sh}) of the devices respectively as listed in Table 2. The lack of efficient excitons dissociating interfaces in the absence of additives result in higher trap-assisted recombination in the blend. This is responsible for the significant difference in device performance. The higher performance of HDT-added devices as compared to PDT-added devices suggests more loss channels in the later. The further loss of V_{oc} on addition of PDT might also be attributed to the higher recombination due aggregation of polymers and its poor interaction with PDT in the blend film which would induce a lower V_{oc} in the OPV devices.

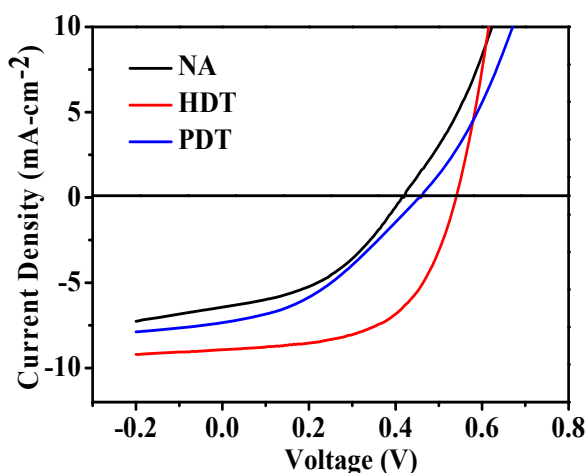


Figure 5. Current density–voltage (J – V) plots for the NA and HDT, PDT-added P3HT:PCBM devices.

Table 2: Electrical performances of NA and HDT, PDT added P3HT:PCBM OSC devices under illumination.

Device/ Parameters	PCE (%)	Jsc (mA/cm ²)	Voc (V)	FF	Rs(k Ω - cm ⁻²)	Rsh (Ω - cm ⁻²)
NA	0.9 \pm 0.2	-6.5 \pm 0.5	0.47 \pm 0.02	0.40 \pm 0.02	24.55	525
HDT	2.7 \pm 0.1	-7.8 \pm 0.3	0.54 \pm 0.01	0.57 \pm 0.01	16.35	1234
PDT	1.6 \pm 0.2	-7.2 \pm 0.5	0.44 \pm 0.02	0.50 \pm 0.02	20.49	760

4. CONCLUSIONS

In conclusion, charge dynamics are revealed by means of ultrafast optical spectroscopy in thiols as additives, in P3HT:PCBM bulk heterojunction solar cells. Although additives enhance the exciton generation in these solar cells, however the recombination dynamics of charge carriers is controlled by the morphology induced by them. The device performance is improved from 0.9% efficient to 2.7% on addition of HDT as an additive in P3HT:PCBM blend solar cells. The carrier dynamics investigated over the temporal regimes spanning (from 1 ps to 5 μ s) reveal the dominance of trap-assisted recombination in non-annealed and PDT-added blend system; however, the additives diminish the recombination in solar cell devices and improve the performance, as validated by extensive electrical measurements. A judicious choice of additives is imperative for performance improvements in bulk heterojunction systems.

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