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## Excitation dynamics of a low bandgap silicon-bridged dithiophene copolymer and its composites with fullerenes

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We report on excitation dynamics in pristine and bulk heterojunction films of the low bandgap silicon-bridged dithiophene copolymer poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] with methanofullerene derivatives. The combination of ultrafast transient transmission and photoluminescence allows us to probe the relaxation of both exciton and polaron states in a relatively wide spectral and temporal range. Measurements reveal that the majority of excitations undergo ultrashort non-radiative relaxation while a small fraction of the photoexcited species decays slowly within hundreds of ps. In the blend films, significantly longer decays are observed suggesting the presence of long lived holes and/or charged-transfer type of excitons. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3703601>]

Over the past two decades, semiconducting polymers have been considered as an alternative to their inorganic counterparts for optoelectronic devices such as light emitting diodes, field-effect transistors, and solar cells, owing to their unique characteristics that allow low cost, solution-processed fabrication into light weight, flexible devices. Significant progress has been demonstrated in solar cells employing bulk heterojunctions of conjugated polymers and fullerenes with power conversion efficiencies approaching the milestone value of 10%.<sup>1</sup> The most commonly utilized donor polymer in such blends has been P3HT; however, its relatively large band gap (1.9 eV) limits the fraction of the solar spectrum that can be harvested and thus the respective solar cell power conversion efficiencies. As a result, there has been an emergence of synthetic efforts to create high performance electron donor polymers that among other desired characteristics possess broad absorption extending to the red and near-IR part of the spectrum.<sup>2-4</sup>

Of particular interest are approaches that explore the use of different linkers to enrich and alter the properties of the material. Si, Ge, or Se has been used to decorate the structures of polymers, replacing carbon atoms and offering a host of possibilities.<sup>5-9</sup> Recently, solar cells based on low bandgap dithiophene donor-acceptor type of copolymers blended with the fullerene derivative PCBM ([6,6]-Phenyl-C61-butyric acid methyl ester) showed efficiencies over 5%.<sup>10</sup> Motivated by studies that demonstrate high carrier mobilities in silicon-containing  $\pi$ -conjugated polymers<sup>11-13</sup> attributed to the high degree of  $\pi$ -delocalization induced by the silicon-bridges, a silole copolymer, poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothia-

diazole)-5,5'-diyl] (labeled Si-PCPDTBT) was synthesized. The copolymer exhibited, high hole mobilities and a broad, structured optical absorption that resulted in bulk heterojunction solar cells with a power-conversion efficiency (PCE) as high as 5.2%.<sup>5,6</sup> Limited studies of the material exist in the literature and those concentrate on the investigation of its basic structural,<sup>6</sup> optical,<sup>5,6</sup> and charge transport<sup>5,6</sup> properties along with studies on the morphology, charge generation, and extraction in the blends of the material with fullerene derivatives.<sup>6,7</sup> It is evident that further studies of the photo-physics of the materials and in particular, an investigation of the ultrafast photo-excitations dynamics of pristine and blend structures that does not exist in the literature can provide insight on processes such as exciton dissociation, recombination and formation of charge transfer or polaron species, which directly influence the solar cell device performance. Here, we performed transient absorption and time-resolved photo-luminescence (TR-PL) spectroscopy on pristine Si-PCPDTBT polymer and Si-PCPDTBT:methanofullerene derivatives (PCBM) bulk heterojunction blends with polymer to fullerene ratios of 1:1, 1:2, and 1:4 using excitation at 3.1 eV (400 nm) and probing in the 2.5-1.25 eV (500–980 nm) spectral range. The two techniques are employed complimentary and allow us to probe both exciton and polaron states at ultrafast timescales. Transient absorption reveals several spectral features associated with state filling and free carrier absorption, which can be described by a three exponential decay function. In pristine polymer, the probed states predominantly decay non-radiatively at ultrafast timescales, while a weaker slower component of the order of hundreds of ps observed both in the transient absorption and photoluminescence (PL) spectra is attributed to radiative recombination. In the blend films, the main variation is the appearance of a much slower component due to the

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presence of long-lived positive polarons (holes) and/or charged-transfer type of excitons.

The polymer material was purchased from Konarka Technologies GmbH and PCBM from Solenne BV. Solutions of the polymer and PCBM were left for overnight stirring separately and mixed 1 h prior to spin casting from CB, with a total weight ratio of 20 mg/ml. Uniform layers of pristine Si-PCPDTBT and Si-PCPDTBT:PCBM blends with ratio of 1:1, 1:2, and 1:4 were deposited at 450 rpm for 75 s. Film thicknesses of around 350 nm were measured with a Dektak profilometer. The films were cast onto quartz substrates for steady state and transient optical absorption measurements. Figure 1 contains the steady-state absorbance of the films along with the PL of the pristine polymer.

The structured main absorbance feature extending down to  $\sim 1.5$  eV is due to strong aggregation effects, which persist even in the blend films, confirming the strong  $\pi$ -stacking of the polymer chains due to the influence of the Si-bridges.<sup>5</sup> Two main peaks at 1.65 eV and 1.8 eV are observed in the spectra of all films, while a third weak shoulder peak at  $\sim 2$  eV is only visible in the pristine polymer. A redistribution of the relative strength of the main peaks going from the pristine to the blend films indicates a corresponding difference in the films aggregation and/or disorder state. The PL spectrum of the pristine film is structured with strong vibronics at  $\sim 1.49$  eV ( $\sim 835$  nm) and  $\sim 1.36$  eV ( $\sim 910$  nm) and a weak third vibronic at  $\sim 1.22$  eV ( $\sim 1020$  nm) that are approximately equidistant in energy ( $\sim 0.13$ – $0.14$  eV). PL from the blends (not shown) is strongly quenched by a factor of 50–100 compared to that of the pristine material indicating efficient interfacial polymer exciton dissociation due to photoinduced electron transfer to PCBM. In the blends PL spectra, the two high energy vibronics appear with almost equal intensities while the relative intensity from the third vibronic appears slightly stronger.

Transient transmission measurements have been carried out using a Ti:Sapphire ultrafast amplifier system generating 100 fs pulses at 800 nm and running at a repetition rate of 1 kHz. A nonlinear crystal was used to generate 400 nm for the purpose of exciting the polymer and blends, whereas part of the fundamental was used to generate a super continuum

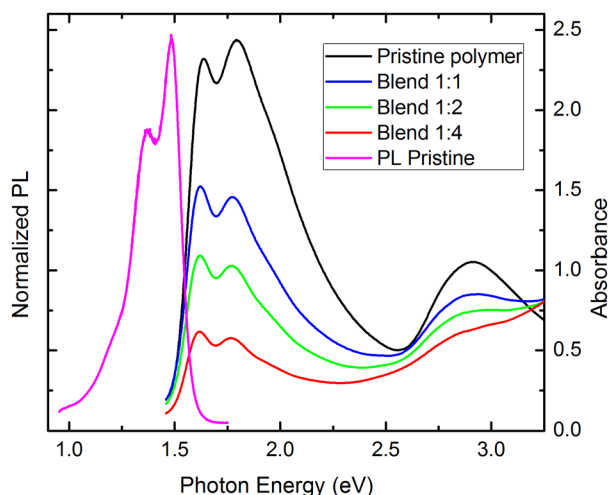


FIG. 1. Absorption and PL of Si-PCPDTBT polymer and Si-PCPDTBT:PCBM bulk heterojunction films.

light for probing different energy states. Measurements were carried out using a typical pump-probe optical setup in a non collinear configuration, where band pass filters were utilized to select the probing photon energy. Typical energy densities incident on the samples were in the range of  $5$ – $50 \mu\text{J}/\text{cm}^2$ . Furthermore, to improve our understanding on the dynamics in the pristine and bulk heterojunction films, TR-PL was carried out using a spectrometer-based time-correlated single photon counting (TCSPC) system equipped with a visible ( $5$ – $1.45$  eV) and a near-infrared ( $1.33$ – $0.8$  eV) photomultiplier tubes with time resolution of  $\sim 30$  and  $\sim 50$  ps, respectively. A laser diode at 3.3 eV (375 nm) operating at 10 KHz was used to excite the luminescence. The repetition rate of both transient absorption and TR-PL was kept on purposely low to avoid significant sample heating/photodegradation during the measurements.

Figure 2 shows differential transmission of pristine Si-PCPDTBT for various probing photon energies covering the range of 1.26 eV to 2.48 eV following excitation at 3.1 eV.

The inset shows the maximum change in differential transmission, which occurs at zero delay between the pump and probe pulse as a function of probing photon energy with several spectral features. There appears to be three positive peaks around 2.0 eV, 1.8 eV, and 1.65 eV. Negative broad features appear at the extremes of the probing range namely at photon energies larger than 2.3 eV and smaller than 1.5 eV. The positive features are predominantly attributed to excitation filling of the singlet exciton states of the pristine polymer and match energetically the corresponding steady state absorption peaks of Figure 1. On the other hand, the broad photoinduced features observed at subgap energies are most probably due to polaron absorptions. The presence and interpretation of the two distinct spectral regions agrees with previous reports on ultrafast studies of the non-Si containing polymer material.<sup>14</sup> Here, we should point out that in all films, the transient transmission signal appeared to be linearly dependent on the excitation density in the range of  $5$ – $50 \mu\text{J}/\text{cm}^2$  employed in this work. This suggests that

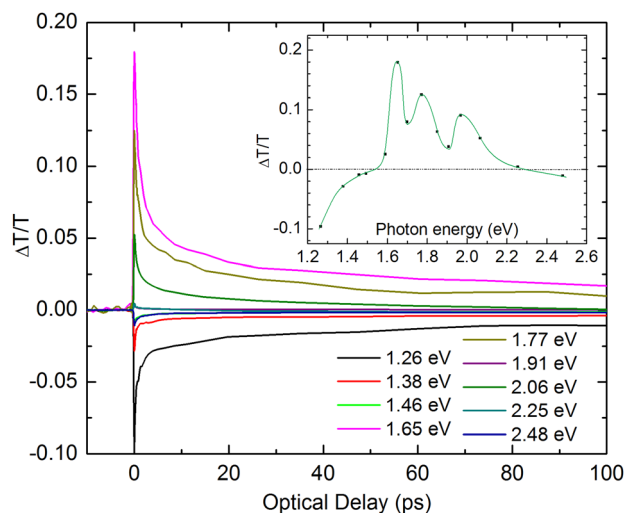


FIG. 2. Transient transmission decays of Si-PCPDTBT polymer at several probing photon energies for excitation at 3.1 eV. The inset shows the  $\Delta T/T$  at zero optical delay where the signal is maximum for the different probing photon energies.

second order relaxation effects are negligible in the experimental data. Furthermore, the signal strength appears to be strongly dependent on the polymer content, which indicates that the majority of the photo-generated species at 3.1 eV are excited in the polymer. Thus, with increasing PCBM content in the blend films, we have a respective decrease in the transient absorption signal. To be able to perform a valid comparative study of all films, the excitation fluence was thus normalized to the steady-state absorption of the films at 3.1 eV, so that the pump photogenerates an approximately equal density of excitations at all samples under study.

The signal in the photo-bleaching region exhibits a fast rise, which is pulse width limited followed by a slower recovery toward equilibrium. Similar behavior is exhibited for the decays dominated by photo-induced absorption. Fitting of the signal recovery for all the probing photon energies requires a 3-exponential function of the form  $A_1e^{-t/t_1} + A_2e^{-t/t_2} + A_3e^{-t/t_3}$  with an ultrafast sub-ps decay  $t_1$ , a fast decay in the range of tens ps, and a longer decay  $t_3$  of hundreds of ps. For the highest photo-bleaching peak at 1.65 eV, the fitting gives  $t_1$  of 0.8 ps (61% amplitude),  $t_2$  of 14.6 ps (29%), and  $t_3$  of 765 ps (10%). Similar values were obtained for the peak at 1.8 eV and 2.0 eV.

The transient transmission results are also supported by TCSPC PL measurements carried out on the films. Typical TR-PL decays from the pristine film and the 1:1 and 1:4 blends are shown at Figure 3, detecting at the vicinity of the first vibronic (1.5 eV) and at the low energy side of the second vibronic (1.3 eV). The decays obtained from the pristine polymer are bi-exponential with a fast component of 100–200 ps and a slower component in the 600–900 ps range. For all probing energies, the decays are dominated by the short component that exhibits a relative amplitude of 80%–90%, in agreement with the transient absorption data. The slow relaxation component corresponding to 10%–20% of the initial occupied states is attributed to radiative recombination of the exciton states while the main part of the occupied states seem to recover non-radiatively within the ultrafast scales measured in the pump-probe data. It is noted

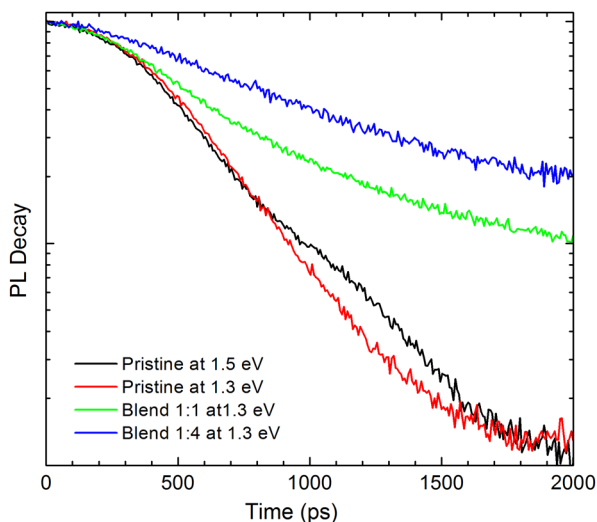


FIG. 3. TR-PL decays from the pristine film and the 1:1 and 1:4 blends probing at the first vibronic (1.5 eV) and at the low energy side of the second vibronic (1.3 eV).

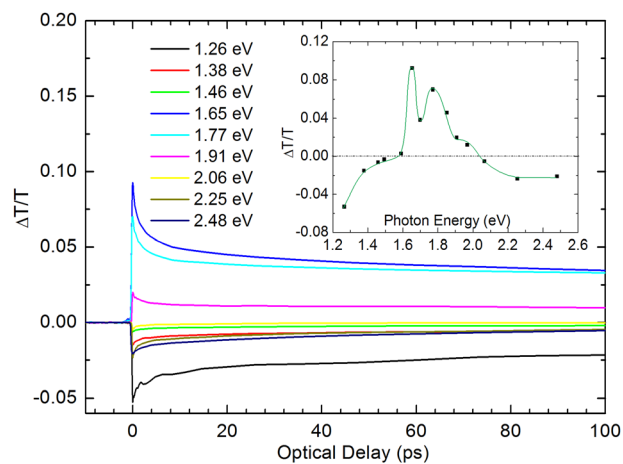


FIG. 4. Transient transmission decays of the Si-PCPDTBT:PCBM (1:4) film at different probe photon energies. The inset shows the  $\Delta T/T$  at zero optical delay for the different probing photon energies.

that previous studies<sup>5</sup> report a mono-exponential polymer exciton lifetime of 65 ps, however those studies employ significant thinner films than those in the present study. A preliminary investigation shows that there exists a significant dependence between the PL excitation dynamics and the polymer film thickness probed. The effect will be addressed by further experiments and will be the topic of future work.

Figure 4 contains the transient transmission of the Si-PCPDTBT:PCBM (1:4) blend, probed at the same energies as those of the pristine polymer. A similar spectral behavior to that of the pristine polymer is observed (see figure inset) while the dynamics are also described by the previously employed triple exponential model. For the highest photo-bleaching peak at 1.65 eV for the 1:4 blend, the fitting gives  $t_1$  of 1 ps (36% amplitude),  $t_2$  of 27 ps (24%), and  $t_3$  of 1.3 ns (40%). Similar values are observed for the 1:1 and the 1:2 blends. As can be readily observed in the comparative Figure 5, the main variation between the pristine material and the blend kinetics is the significantly larger contribution of the longer time constant  $t_3$ , with values in the range of 1–2 ns. Furthermore, at several probe wavelengths, the long decay

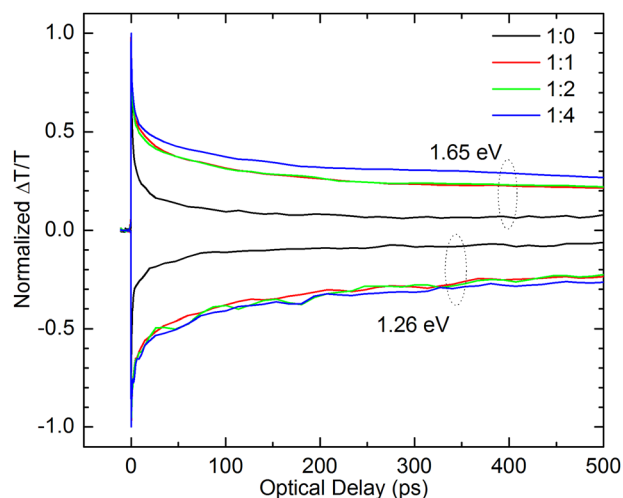


FIG. 5. Normalized transient transmission decays of the Si-PCPDTBT polymer (1:0) and the Si-PCPDTBT:PCBM blends (1:1, 1:2, and 1:4) film at different probe photon energies.



contribution scales with PCBM content whilst a similar trend is present in the TR-PL measurements (see Figure 3), where the long recombination lifetime almost doubles (1.4–1.8 ns) and its relative amplitude almost triples compared to the respective values for the pristine polymer.

Based on previous studies,<sup>14</sup> the observation of such long lived species in the transient spectra typically points towards the presence of positive polarons (holes) or charged-transfer type of excitons<sup>15</sup> formed subsequently to electron transfer from the polymer to PCBM. Recent investigations<sup>6</sup> indicate a low yield formation of charged-transfer excitons in Si-PCPDTBT:PCBM blends. However, the fact that the long lived decays are also present in the PL dynamics points towards an emissive species i.e., excitons instead of holes. Furthermore, the stronger relative emission from the longer wavelength vibronics in the blends relative to the pristine material can also be indicative of the presence of such species. Of course, the possibility that pump-probe and TR-PL probe a mixture of long lived holes and charged-transfer species cannot be ruled out.

Concluding, we have studied the excitations dynamics in pristine and bulk heterojunction films with PCBM based on the low bandgap copolymer Si-PCPDTBT using a combination of time-resolved absorption and luminescence techniques. Ultrafast transient transmission in the pristine polymer reveals a three-exponential relaxation with a sub-ps decay, a fast decay in the range of tens of ps, and a longer decay of hundreds of ps. The great majority of the excitations (~90%) relax non-radiatively via the two fast components. The weaker slow decay appears in both transient absorption and PL data with almost identical kinetics and relative amplitudes and it is attributed to radiative recombination of the exciton states. Si-PCPDTBT:PCBM blends with various polymer to PCBM ratios reveal dynamics with similar spectral and temporal characteristics to the pristine film up to the range of tens of ps. However, at longer times, a significantly larger contribution from the slower relaxation component with significantly longer decays up to 2 ns is observed, indicating the presence of new species different from those observed in the pristine film. Based on previous studies<sup>6</sup> that indicate a low efficiency in the formation of interfacial charge transfer excitons in blends based on Si-PCPDTBT,

the long lived species could be predominantly attributed to positive polarons (holes). However, the clear presence of the long decays in the blend PL dynamics cannot decisively ruled out the presence of charged-transfer excitons instead or in addition to holes at longer delays.

Our future work on the Si-PCPDTBT:PCBM material system includes the exploitation of sophisticated transient optical techniques such as terahertz spectroscopy, which should be a suitable experimental tool to distinguish between charged and neutral excitation species (such as excitons).

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