

## Dramatic enhancement of photo-oxidation stability of a conjugated polymer in blends with organic acceptor

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Photo-oxidation of a prototype conjugated polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) in blended films with 2,4,7-trinitrofluorenone (TNF) is drastically suppressed upon exposure to green laser radiation under ambient conditions that was observed by using Fourier transform infrared spectroscopy. By increasing the TNF concentration in MEH-PPV, we have found that the photo-oxidation rate and the photoluminescence intensity drop together in a correlated way by three orders of magnitude. We suggest that triplet exciton formation in the MEH-PPV/TNF blends is deeply suppressed blocking the photo-oxidation. These findings may open a way to intrinsically photostable conjugated polymer materials for photonic and photoelectric applications. © 2008 American Institute of Physics. [DOI: 10.1063/1.2945801]

Conjugated polymers promise wide applications in various photonic and electronic devices. However, one of the basic drawbacks of conjugated polymers is their poor photo-oxidation stability under ambient conditions.<sup>1-5</sup> In polymer solar cells, photo-oxidation effects in the active layer give one of the main contributions to their degradation.<sup>6</sup> To reduce photo-oxidation in polymer devices, encapsulation techniques are currently used. However, standard encapsulation techniques are insufficient to block oxygen contamination completely and are hardly compatible with the devices fabricated on flexible substrates. Therefore, intrinsically photostable conjugated polymer materials are strongly demanded. Blends of conjugated polymers with fullerenes are now actively studied as materials for photoelectric applications such as solar cells and photodetectors. Notably, the polymer in such a blend can have enhanced photo-oxidation stability: the photo-oxidation rate (PR) of polyphenylenevinylene (PPV) soluble derivatives blended with fullerenes is slowed down by an order of magnitude as compared to that of the pristine polymer.<sup>7-9</sup> Fast electron transfer from the photoexcited PPV derivative to the fullerene was supposed to strongly inhibit the formation of triplet excited states at the polymer so that highly reactive singlet oxygen cannot be generated.<sup>7</sup>

In this work, we demonstrate that the PR of a prototype conjugated polymer, poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), in a donor-acceptor blend can be substantially lower than that observed previously in polymer/fullerene blends.<sup>7-10</sup> Motivated by recent observation of slowing down the MEH-PPV photobleaching rate upon addition of 2,4,7-trinitrofluorenone (TNF) to MEH-PPV,<sup>11</sup> we have studied Fourier transform infrared (FTIR) spectra of MEH-PPV/TNF blends under both visible irradiation and ambient conditions. According to our data,

the MEH-PPV PR in blends with TNF drops by three orders of magnitude as compared to the pristine MEH-PPV. We have observed that the MEH-PPV PR and its photoluminescence (PL) decrease in a correlated way upon increasing the acceptor concentration in the blend. We show that these observations are in agreement with earlier findings indicating that triplet excited states are the main precursors for photo-oxidation of conjugated chains.<sup>12-14</sup> Therefore, if the triplet excitons do not form, one can expect enhanced photostability. We suggest that such a drastic enhancement of photostability in the studied donor-acceptor blends is associated with a ground-state charge-transfer complex (CTC) formed between MEH-PPV and TNF.<sup>15,16</sup> This CTC can strongly quench the singlet excitons at the polymer blocking the singlet-triplet relaxation pathway and, hence, the triplet generation. Remarkably, such a conjugated polymer CTC could be an interesting low-band-gap material for photonic and photoelectric applications due to its considerable absorption and photoelectric sensitivity in the red/near-IR spectral range.<sup>17</sup>

MEH-PPV (Sigma-Aldrich) was dissolved in chlorobenzene at concentration 2 g/l for 90 min at 60 °C. Films of MEH-PPV/TNF blends on BaF<sub>2</sub> or glass substrates were prepared by drop casting the chlorobenzene solution with MEH-PPV:TNF molar ratio from 1:0.0001 to 1:0.4 per polymer monomer unit. To study the photo-oxidation stability of MEH-PPV/TNF films under ambient conditions, we recorded evolution of their FTIR spectra under continuous-wave green irradiation. The MEH-PPV/TNF films on BaF<sub>2</sub> substrates were exposed to radiation at a wavelength of 532 nm with an intensity of 330 mW/cm<sup>2</sup> from the side of air-film interface under ambient conditions. All the pump radiation was absorbed by the films at the beginning of irradiation, and the polymer films with zero or low content of TNF showed photobleaching during irradiation. FTIR measurements were carried out by using an Infracum FT-810 spectrometer (Simex). Transmission spectra were recorded with a 1 cm<sup>-1</sup> resolution and averaged over 4 min. We recorded the initial spectra before irradiation, and then the

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spectra were recorded during irradiation. PL of the polymer films was measured in the backscattering geometry under ambient conditions. The PL signal was dispersed using a monochromator with additional filters and was recorded using a Si detector and a lock-in amplifier. To record the PL, the samples were excited at a wavelength of 532 nm with a maximum intensity of 50 mW/cm<sup>2</sup>. The shapes of all the PL spectra were identical excluding the sample with the highest TNF content (1:0.4), for which the PL was below the noise level. To take into account the possible photodegradation effect during recording the PL spectra, we recorded a set of PL spectra successively and compared them. This effect could decrease the PL by no more than 10%–15% for pristine MEH-PPV films showing the highest PL photodegradation effect.

Exposure of PPV-type polymers to visible light in the presence of oxygen is known to result in their fast photo-oxidation. As was observed earlier,<sup>3,7,8</sup> all the strong IR bands of alkoxy-substituted PPVs in the range of 800–1500 cm<sup>-1</sup> gradually decrease during irradiation. The irradiation results also in appearing bands at 1600, 1678, and 1732 cm<sup>-1</sup> indicating photo-oxidation of the polymer. The two latter are assigned to the carbonyl group of the photo-oxidation products.<sup>1,18,19</sup> Our experiments show that doping of MEH-PPV by TNF essentially slows down the polymer photo-oxidation. We discuss here the only band of the MEH-PPV backbone at 966 cm<sup>-1</sup> assigned to the out-of-plane wagging vibration of vinylene CH (Ref. 20) because this mode is very sensitive to  $\pi$ -conjugation,<sup>21</sup> and its decrease is usually attributed to the loss of  $\pi$ -conjugation.<sup>18,19</sup> Moreover, we noted that the band at 966 cm<sup>-1</sup> decreases faster than other characteristic modes of the PPV backbone (e.g., 1415 and 1506 cm<sup>-1</sup>) during irradiation.

Figure 1 presents changes in the integral intensity of the absorption bands at 966, 1678, and 1732 cm<sup>-1</sup> as a function of irradiation time for different TNF concentrations. To obtain the integral absorption intensity, we deconvoluted the FTIR spectra around these bands into three to ten Lorentzians. Among these Lorentzians, we selected a set corresponding to a certain IR band and calculated the area under the selected Lorentzians. As seen in Fig. 1, even 0.1 mol % of TNF noticeably slows down photo-oxidation, and 3 mol % of TNF decreases its rate by an order of magnitude: the 966 cm<sup>-1</sup> band decreases slower [Fig. 1(a)], and the 1678 and 1732 cm<sup>-1</sup> bands increase slower [Figs. 1(b) and 1(c)]. Moreover, for the 1:0.4 MEH-PPV/TNF blend, the intensity of the 966 cm<sup>-1</sup> band remains constant within our experimental error after almost 6 h of irradiation [Fig. 1(a)]. At the same time, the bands of photo-oxidation products (1678 and 1732 cm<sup>-1</sup>) increase very slowly as seen in Figs. 1(b) and 1(c).

To compare very dissimilar photo-oxidation behavior of different MEH-PPV/TNF blends, we calculated the PR as a slope for each curve in Fig. 1 at the beginning of the irradiation. The data in Fig. 1 were fitted according to a model analogous to that presented in Refs. 22 and 23 by a function  $\Delta\text{Abs}(t) = A \exp(t/B) + C$ , where  $A$ ,  $B$ , and  $C$  are fitting parameters. The PR was calculated as the ratio  $A/B$ , i.e., the slope at  $t=0$ . Figure 2 compares the PR for bands at 966, 1678, and 1732 cm<sup>-1</sup> in MEH-PPV/TNF blends for different acceptor concentrations. It is seen that the PR of all the bands decreases by about three orders of magnitude in the 1:0.4 MEH-PPV/TNF blend as compared to the pristine

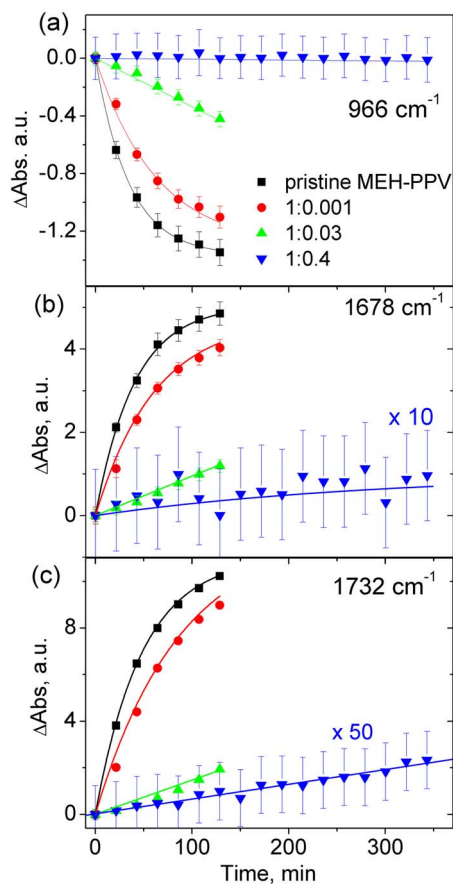


FIG. 1. (Color online) Difference in the integral absorption,  $\Delta\text{Abs}(t) = \text{Abs}(t) - \text{Abs}(0)$ , of the bands at 966 cm<sup>-1</sup> (a), 1678 cm<sup>-1</sup> (b), and 1732 cm<sup>-1</sup> (c) as a function of irradiation time  $t$  for blends with different MEH-PPV:TNF ratios. The data in panels (b) and (c) for the blend with maximum TNF content (1:0.4) are multiplied by a factor of 10 and 50, respectively. The solid lines show exponential fitting functions.

polymer. As seen in Figs. 1 and 2, the dynamic range of the PRs is limited mainly by the experimental error except the band at 1732 cm<sup>-1</sup>, for which the minimum PR was obtained with an error less than 10%. According to the data for the band at 1732 cm<sup>-1</sup>, the PR falls by a factor of 1800 in the MEH-PPV/TNF blend as compared to the pristine MEH-PPV.

We have observed that the MEH-PPV PL intensity and its PR decrease with increasing TNF concentration in a correlated way, and both decrease by about three orders of magnitude as compared to the pristine MEH-PPV (Fig. 2). This correlation can be explained as follows. Triplet excited states

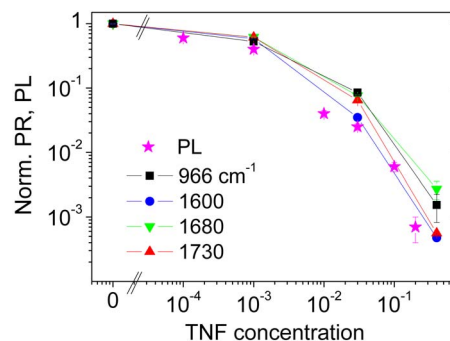


FIG. 2. (Color online) Normalized PR for different IR bands and PL of MEH-PPV/TNF blends vs TNF molar concentration.

of conjugated chains are generally believed to be the key intermediates in their photo-oxidation. The destructive interaction of triplet excited PPV conjugated chains with oxygen can occur in a number of ways,<sup>14</sup> one of which includes generation of singlet oxygen.<sup>12</sup> Therefore, it is reasonable to suggest that the PR is proportional to the density of the triplet excitons. If the triplets are formed via intersystem crossing from the singlets, their densities are proportional. As a result, the PL intensity determined by the density of singlets is expected to be proportional to the PR determined by the density of triplets.

After photoexcitation, MEH-PPV singlet excitons are transformed into triplet ones via relatively slow intersystem crossing competing with radiative (PL) and other nonradiative relaxation pathways. With increasing the acceptor concentration, the latter become dominant nearly blocking the singlet-triplet pathway; hence, the triplet states cannot be populated. This is supported by our photoinduced absorption data showing the absence of triplet-triplet absorption in MEH-PPV/TNF blends.<sup>17</sup> Thus, our data confirm earlier findings that quenching triplet excitons<sup>5,14</sup> or blocking their formation<sup>7,8</sup> could be an efficient means to slow down photo-oxidation of PPVs.

Efficient PL quenching in MEH-PPV/TNF blends could be associated with an easily observable CTC between the blend components in the electronic ground state.<sup>15,16</sup> The CTC absorption band overlaps with the MEH-PPV PL band so that fast energy transfer from the MEH-PPV to the CTC is possible. This energy transfer could compete with donor-acceptor electron transfer, which is a generally accepted PL quenching mechanism in polymer/fullerene blends. Moreover, the ground-state charge-transfer interaction between MEH-PPV and TNF could facilitate miscibility of film's components resulting in a more homogeneous distribution of acceptor molecules in the polymer matrix<sup>24</sup> that could be an additional factor enhancing PL quenching.

On the other hand, deep PL quenching is insufficient for high photo-oxidation stability. Actually, conjugated polymer/fullerene blends can show almost complete quenching of the polymer PL.<sup>25</sup> However, the PR decreases by only about one order of magnitude as compared to the pristine polymer<sup>7-9</sup> and is limited by photo-oxidation of the fullerene.<sup>8,9</sup> Probably, photo-oxidation of polymer/fullerene blends is mainly controlled by the triplet states forming at the fullerene. Absorbing visible light, fullerenes are known to be efficient photosensitizers of singlet oxygen,<sup>26</sup> which can oxidize the polymer.<sup>12</sup> The optical gap of TNF is higher than the energy of irradiating photons that excludes the appearance of triplets at the acceptor and, therefore, their possible contribution to photo-oxidation.

In conclusion, we have demonstrated a dramatic increase in photo-oxidation stability of MEH-PPV in blends with TNF under both green irradiation and ambient conditions. The MEH-PPV PR and PL in the blends decrease together by three orders of magnitude. We suggest that the MEH-PPV triplet excitons are one of the main precursors for photo-oxidation of the blends and blocking their formation can strongly enhance the photostability. The observed photostability enhancement in MEH-PPV/TNF blends is probably as-

sociated with a CTC formed between MEH-PPV and TNF in the electronic ground state. In addition, the polymer CTC is a low-band-gap material with essential optical absorption in the red and near-IR spectral ranges<sup>15</sup> that is important for photoelectric applications. Thus, our data suggest that blending of a PPV-type polymer with an appropriate acceptor strongly quenching the polymer PL may be an efficient means of enhancing the photo-oxidation stability up to the level sufficient for practical applications in photonics and electronics.

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