

# Organic semiconductor composites: Influence of additives on the transient photocurrent

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We report on the effect of various guest molecules added to a functionalized anthradithiophene (ADT) host on photoexcited charge carrier dynamics in solution-deposited thin films, from  $\sim 100$  ps to  $>100$   $\mu$ s after photoexcitation with 100 fs laser pulses. An addition of 2 and 5 wt % of C<sub>60</sub> to a fluorinated ADT derivative, ADT-TES-F, resulted in transient photocurrent amplitude enhancement by a factor of  $\sim 3$  and 10, respectively. In contrast, an addition of 10 wt % of another ADT derivative, ADT-TIPS-CN, or a functionalized pentacene derivative (TIPS pentacene) to ADT-TES-F led to a decrease in the amplitude by a factor of  $\sim 3$ –4 and dramatically different photocurrent dynamics. © 2009 American Institute of Physics. [DOI: 10.1063/1.3062850]

Organic semiconductors have attracted considerable attention due to their potential applications in low-cost and/or large-area (opto)electronic devices.<sup>1</sup> Solution-processable materials can be tailored for specific applications by creating mixtures of various derivatives, thus tuning optical and electronic properties of the resulting composites. While polymer composites have been extensively studied,<sup>2,3</sup> composites based on small molecular weight materials have not been explored to the same extent due to reduced solubility of many high-performance compounds, thus requiring, for example, thermal coevaporation in vacuum, which limits practical use of such composites.<sup>4,5</sup> Recently, a variety of high-performance solution-processable functionalized pentacene and anthradithiophene (ADT) derivatives have been synthesized and characterized.<sup>6</sup> Charge carrier mobilities over 1 cm<sup>2</sup>/V s have been reported in spin-coated and drop-cast thin films of several derivatives including a fluorinated ADT derivative used in our study.<sup>7–9</sup>

In this letter, we examine the effects of addition of different guest molecules to a fluorinated ADT host on the photoexcited charge carrier dynamics observed in solution-deposited thin films at time-scales from  $\sim 100$  ps to over 100  $\mu$ s after excitation with 100 fs laser pulses. Differences in amplitudes and dynamics of the transient photocurrent depending on the composite suggest that photoexcited charge carrier dynamics can be effectively manipulated, even at short time scales, by optimizing a composite for particular applications, including those relying on ultrafast carrier generation and transport.<sup>10,11</sup> Introducing guest molecules also provides a way to better understand the nature of transient photoresponse in functionalized ADT derivatives, as well as the physical mechanisms which contribute to transient photocurrent decay dynamics.

In our studies, we explored thin films of fluorinated ADT derivative functionalized with triethylsilylethynyl (TES) side groups (ADT-TES-F), both pristine and doped with C<sub>60</sub>, with a pentacene derivative functionalized with tri-isopropylsilylethynyl (TIPS) side groups, or with another ADT derivative (ADT-TIPS-CN) [Fig. 1(a)].<sup>8,12,13</sup> Each of

the compounds was dissolved in toluene. Various mixtures of these solutions were then prepared to yield the following compositions: (i) ADT-TES-F/C<sub>60</sub>, with C<sub>60</sub> added at the concentration of 2, 5, or 10 wt %, (ii) ADT-TES-F (90 wt %)/TIPS pentacene (10 wt %), and (iii) ADT-TES-F (90 wt %)/ADT-TIPS-CN (10 wt %). The mixtures were drop cast onto glass substrates prepatterned with Cr (5 nm)/Au (50 nm) interdigitated electrodes (ten finger pairs with a finger length of 1 mm, a width of 25  $\mu$ m, and with a 25  $\mu$ m gap between the fingers) at 60 °C, yielding polycrystalline films.<sup>12,13</sup>

The relative positions of highest occupied and lowest unoccupied molecular orbital levels (HOMO and LUMO, respectively) of the molecules used here, which guided our

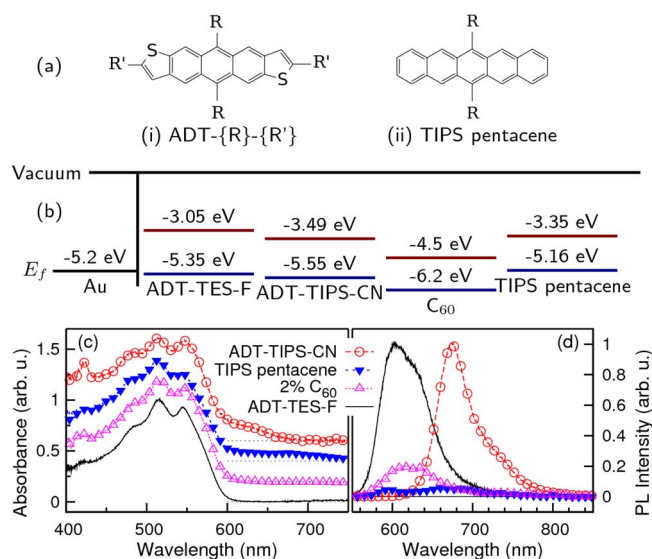


FIG. 1. (Color online) (a) Molecular structures used in our studies. R=TES or TIPS, R'=F or CN in ADT derivatives and R=TIPS in the pentacene derivative. (b) Energy level diagram for the ADT-TES-F, ADT-TIPS-CN, TIPS pentacene molecules (from Ref. 13), as well as C<sub>60</sub> (Ref. 14). (c) Absorption and (d) PL spectra of thin films of pristine ADT-TES-F and ADT-TES-F/ADT-TIPS-CN, ADT-TES-F/TIPS pentacene, and ADT-TES-F/C<sub>60</sub> (2%) composites. Absorption spectra are shifted along the y axis for clarity.

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choice of the composites, are given in Fig. 1(b). In particular, in the ADT-TES-F/ $C_{60}$  composite,  $C_{60}$  [Fig. 1(b)]<sup>10,14</sup> was expected to act as an acceptor [Fig. 1(b)], similar to its role in polymer composites and organic glasses doped with fullerenes to promote charge photogeneration.<sup>3,15–17</sup> Qualitatively, ADT-TIPS-CN in ADT-TES-F/ADT-TIPS-CN composite could play a role similar to  $C_{60}$  but with much less disruption in molecular packing compared to  $C_{60}$ , due to similarity of structures of ADT-TES-F and ADT-TIPS-CN. In contrast, TIPS pentacene would create an electron and a hole trap with depths of 0.3 and 0.19 eV, respectively, in addition to serving as a potential site for energy transfer from ADT-TES-F.<sup>5,18</sup> Therefore, the photoexcited charge carriers in the chosen composites would face different charge-transfer environments, which we sought to explore on short time scales after photoexcitation.

Figure 1(c) shows absorption spectra of the composite films. These were additions of the spectra of the constituents<sup>11,13</sup> with no charge transfer bands apparent with the sensitivity of our spectrometer (Ocean Optics USB2000). This indicates no significant interactions between the constituents of our composites in the ground state. In all composites, most of the 400 nm light used in our transient photocurrent measurements was absorbed by ADT-TES-F. Changes in relative vibronic peak amplitudes in the absorption spectra of the composites are due to film-to-film variation in morphology and influence of guest molecules on the molecular packing.<sup>13</sup>

Photoexcited charge carrier dynamics were examined using an amplified Ti:sapphire laser (100 fs, 800 nm, 1 kHz), combined with a frequency-doubling beta-barium borate crystal to excite the samples with a wavelength of 400 nm with fluences in the range between 5 and 10  $\mu\text{J}/\text{cm}^2$ . Voltage in the range between 20 and 100 V was applied to the samples using a Keithley 237 source-measure unit and a 50 GHz digital sampling oscilloscope was used to detect the photocurrent with a time resolution of  $\sim 100$  ps.<sup>12</sup> In the same samples, photoluminescence (PL) was excited with a Nd:YVO<sub>4</sub> continuous wave laser at a wavelength of 532 nm, and emission spectra [Fig. 1(d)] were recorded using an Ocean Optics USB2000 spectrometer.<sup>13</sup> Experiments were performed in air at room temperature ( $\sim 23$  °C).

Transient photocurrents (due to photogenerated holes moving under applied electric field),<sup>12</sup> normalized at their peak values, obtained in pristine ADT-TES-F and in ADT-TES-F/ $C_{60}$  (2%) films are shown in Fig. 2. In both samples, the rise of the photocurrent ( $I_{\text{ph}}$ ) was fast, limited by the time resolution of the setup, and the decay dynamics were characterized by a fast initial decay component followed by a slow one that lasted up to at least 1 ms.<sup>12,13,19</sup> In samples containing  $C_{60}$ , the initial decay was faster than in pristine ADT-TES-F, suggestive of more efficient charge trapping and recombination within the first  $\sim 100$  ps after photoexcitation (limited by time resolution of our setup) in ADT-TES-F/ $C_{60}$  composites, with a more pronounced contribution to the overall decay dynamics. For example, in Fig. 2, at 5 ns after photoexcitation,  $\sim 50\%$  of “initially” photogenerated carriers (i.e., without taking into account trapping and recombination occurring at times below our time resolution)<sup>11,12</sup> were mobile in pristine ADT-TES-F, while only 27% of carriers remained mobile in ADT-TES-F/ $C_{60}$  (2%). Upon increasing the concentration of  $C_{60}$ , this initial

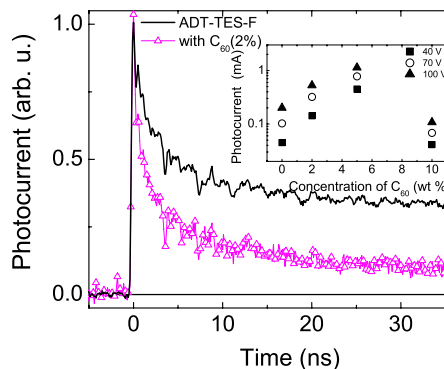


FIG. 2. (Color online) Transient photocurrent normalized at its peak value obtained in pristine ADT-TES-F film and at ADT-TES-F/ $C_{60}$  (2%) composite under photoexcitation with 400 nm 100 fs laser pulse. Inset shows amplitudes of the transient photocurrent as a function of concentration of  $C_{60}$  in ADT-TES-F/ $C_{60}$  composites, measured at 40, 70, and 100 V at a fluence of 5  $\mu\text{J}/\text{cm}^2$ .

decay became even more pronounced, with only 18% of initially photogenerated carriers remaining mobile at 5 ns after excitation of ADT-TES-F/ $C_{60}$  (10%). The slow component of the decay dynamics could be described by a power-law function ( $I_{\text{ph}} \sim t^{-\beta}$ ) over many orders of magnitude in time (Refs. 11–13 and inset of Fig. 3), with  $\beta \sim 0.2–0.3$  in pristine ADT-TES-F films and  $\beta \sim 0.1$  in samples containing  $C_{60}$  (e.g.,  $\beta = 0.108 \pm 0.009$  in the inset of Fig. 3). Slowing down of the decay dynamics upon addition of  $C_{60}$  has been previously observed in polymer composites and attributed to reduced charge recombination due to spatial separation of the holes and electrons.<sup>20</sup> In our case, the spatial separation of the holes and electrons on ADT-TES-F and  $C_{60}$ , respectively, reduced charge recombination at times longer than  $\sim 10$  ns.

The inset of Fig. 2 shows a peak amplitude of the transient photocurrent as a function of concentration of  $C_{60}$  in the ADT-TES-F/ $C_{60}$  composite, at 40, 70, and 100 V. Addition of  $C_{60}$  at a concentration of 2 and 5% increased the photocurrent amplitude by a factor of  $\sim 3$  and 10, respectively, at 40 V. This increase is most likely due to fast photoinduced electron transfer (a mechanism similar to that leading to sensitization of  $C_{60}$ -containing polymer composites and organic glasses),<sup>3,15–17</sup> a conclusion based on our observation of sig-

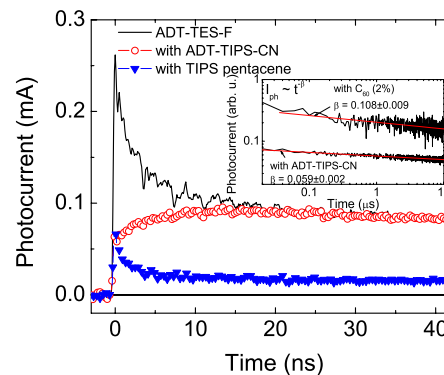


FIG. 3. (Color online) Transient photocurrent obtained in pristine ADT-TES-F film and in ADT-TES-F/TIPS pentacene and ADT-TES-F/ADT-TIPS-CN composites at a fluence of 5  $\mu\text{J}/\text{cm}^2$  at 100 V. Inset shows longer time-scale dynamics of the transient photocurrent obtained in ADT-TES-F/ $C_{60}$  (2%) and ADT-TES-F/ADT-TIPS-CN composites. Power-law decay fits ( $I_{\text{ph}} \sim t^{-\beta}$ ) are also shown. The transients are shifted along y axis for clarity.

nificant PL quenching in ADT-TES-F/ $C_{60}$  composite films, compared to pristine ADT-TES-F films [Fig. 1(d)]. Further addition of  $C_{60}$  lowered the measured photocurrent amplitude (e.g., by a factor of  $\sim 2$  at 10% of  $C_{60}$ , at 100 V), most likely due to enhanced initial recombination, occurring at times below  $\sim 100$  ps, not resolved in our experiments.

Addition of either TIPS pentacene or ADT-TIPS-CN to ADT-TES-F lowered the amplitude of the transient photocurrent by a factor of  $\sim 3$ – $4$  at all applied voltages in the range studied. The most interesting effect of adding these molecules to the ADT-TES-F host was, however, the change in the initial photocurrent decay dynamics (Fig. 3). In particular, upon addition of TIPS pentacene, the initial decay became faster, the effect similar to that achieved by the addition of  $C_{60}$ . For example, only  $\sim 32\%$  of initially photogenerated carriers remained mobile at 5 ns after photoexcitation in the ADT-TES-F/TIPS pentacene composite. From Fig. 1(d), addition of TIPS pentacene significantly quenched PL of ADT-TES-F, while no energy transfer to TIPS pentacene was detected. In conjunction with the photocurrent data in Fig. 3, this would be consistent with fast hole transfer from ADT-TES-F to TIPS pentacene, followed by trapping at the TIPS pentacene molecules.<sup>21</sup> At times longer than 10 ns, the photocurrent decay was similar to that observed in pristine ADT-TES-F films, with the power-law exponent  $\beta \sim 0.2$ . In contrast, addition of ADT-TIPS-CN to ADT-TES-F introduced a slow component into the photocurrent rise dynamics and completely removed the fast initial decay (Fig. 3). In particular, the fast rise of the photocurrent, limited by the time resolution of our setup, accounted only for  $\sim 70\%$  of all photogenerated carriers, whereas the other 30% were generated over  $\sim 0.1$ – $20$  ns. As a result, the peak of the photocurrent in the ADT-TES-F/ADT-TIPS-CN composite was achieved at about 20 ns after photoexcitation, after which a slow decay, characterized by a power-law function with  $\beta < 0.1$  (e.g.,  $\beta = 0.059 \pm 0.002$  in the inset of Fig. 3), persisted to at least 1 ms after photoexcitation. Our observations of complete PL quenching of the ADT-TES-F, while magnifying PL of the ADT-TIPS-CN [Fig. 1(d)] (Ref. 13) in the ADT-TES-F/ADT-TIPS-CN composite suggest efficient energy transfer from ADT-TES-F to ADT-TIPS-CN.<sup>14,22</sup> Therefore, it is possible that the slow component in the rise dynamics of the transient photocurrent in Fig. 3 is due to a multistep process that involves excitation of ADT-TES-F, followed by energy transfer to ADT-TIPS-CN, which then leads to energetically favorable hole transfer back to ADT-TES-F, while the electron remains trapped on the ADT-TIPS-CN molecules. The spatial separation of the electron and hole would then account for the reduced probability of charge recombination, manifested through a much slower photocurrent decay dynamics at long time-scales, as compared to pristine ADT-TES-F.

In summary, we examined the contribution of several guest molecules added to the functionalized ADT host, ADT-TES-F, to photoexcited charge carrier dynamics on time-

scales from  $\sim 100$  ps up to over  $100 \mu\text{s}$  after photoexcitation. Addition of 2 and 5 wt % of  $C_{60}$  led to an increase in the amplitude of the transient photocurrent by a factor of  $\sim 3$  and 10, respectively, while increasing initial ( $< 100$  ps) charge trapping and recombination and inhibiting long time-scale ( $> 100$  ns) recombination. Addition of ADT-TIPS-CN dramatically changed photocurrent dynamics by introducing an additional, slow photogeneration process and reduced carrier recombination. In contrast, addition of TIPS pentacene led to a more pronounced initial decay of the photocurrent, possibly due to fast hole trapping.

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