Charge carrier dynamics in organic semiconductors and their donor-acceptor composites: Numerical modeling of time-resolved photocurrent

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We present a model that describes nanosecond (ns) time-scale photocurrent dynamics in functionalized anthradithiophene (ADT) films and ADT-based donor-acceptor (D/A) composites. By fitting numerically simulated photocurrents to experimental data, we quantify contributions of multiple pathways of charge carrier photogeneration to the photocurrent, as well as extract parameters that characterize charge transport (CT) in organic films including charge carrier mobilities, trap densities, hole trap depth, and trapping and recombination rates. In pristine ADT films, simulations revealed two competing charge photogeneration pathways: fast, occurring on picosecond (ps) or sub-ps time scales with efficiencies below 10%, and slow, which proceeds at the time scale of tens of nanoseconds, with efficiencies of about 11%–12%, at the applied electric fields of 40–80 kV/cm. The relative contribution of these pathways to the photocurrent was electric field dependent, with the contribution of the fast process increasing with applied electric field. However, the total charge photogeneration efficiency was weakly electric field dependent exhibiting values of 14%–20% of the absorbed photons. The remaining 80%–86% of the photoexcitation did not contribute to charge carrier generation at these time scales. In ADT-based D/A composites with 2 wt.% acceptor concentration, an additional pathway of charge photogeneration that proceeds via CT exciton dissociation contributed to the total charge photogeneration. In the composite with the functionalized pentacene (Pn) acceptor, which exhibits strong exciplex emission from a tightly bound D/A CT exciton, the contribution of the CT state to charge generation was small, ~8%–12% of the total number of photogenerated charge carriers, dependent on the electric field. In contrast, in the composite with PCBM acceptor, the CT state contributed about a half of all photogenerated charge carriers. In both D/A composites, the charge carrier mobilities were reduced and trap densities and average trap depths were increased, as compared to a pristine ADT donor film. A considerably slower recombination of free holes with trapped electrons was found in the composite with the PCBM acceptor, which led to slower decays of the transient photocurrent and considerably higher charge retention, as compared to a pristine ADT donor film and the composite with the functionalized Pn acceptor.

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I. INTRODUCTION

Organic donor-acceptor (D/A) composites are of interest for applications in solar cells, lasers, photodetectors, and photorefractive devices due to enhanced charge carrier photogeneration resulting from the photoinduced charge transfer (CT) between the donor (D) and acceptor (A) molecules. While currently most high-performance bulk heterojunctions (BHJs) are based on polymer/fullerene composites, performance of small-molecule BHJs (SMBHJs), which are still relatively unexplored, is rapidly improving, with several SMBHJ-based solar cells exhibiting power conversion efficiencies of 6%–7%. In order to further improve performance of BHJs, including SMBHJs, it is important to understand mechanisms of charge carrier photogeneration, transport, and recombination, as well as their contribution to the photocurrent, in both pristine organic semiconductor materials and their D/A composites. Many recent studies have addressed dynamics and propensity for dissociation of CT states, effects of D/A LUMO and HOMO energy offsets, and of D/A molecular packing at the D/A interfaces, in polymer-based BHJs, whereas relatively few studies have explored similar issues in SMBHJs. For SMBHJs, of particular interest are solution-processable photoconductive organic semiconductors with high charge carrier mobilities and solid-state packing favoring efficient charge separation at the D/A interfaces. Examples of such materials are functionalized pentacene (Pn) and anthradithiophene (ADT) derivatives which exhibit thin-film charge carrier (hole) mobilities of above ~1.5 cm²/(Vs), fast photore-
films is that experimentally measured photocurrents include contributions of a variety of processes that are challenging to disentangle, so that several different experimental techniques need to be applied to the same film in order to study each process separately. Numerical modeling of the photocurrent dynamics may provide a valuable insight into the relative contribution of each process to the photocurrent, thus avoiding multiple experiments. A considerable amount of such work has been done in polymer-based films, including Monte Carlo simulations of hopping conduction of photoexcited carriers, numerical modeling of the time-resolved photocurrent dynamics on various timescales, and modeling of the photocurrent in solar cells.

In this paper, we present numerical modeling of nanosecond (ns) time-scale time-resolved photocurrent dynamics in ADT films and ADT-based D/A composites. For our studies, we chose a fluorinated ADT derivative functionalized with triethylisilylthienyl (TES) side groups, ADT-TES-F, as the donor and either PCBM or a fluorinated Ph derivative (Pn-TIPS-F8) functionalized with triisopropylsilylthiophenyl (TIPS) side group as acceptors (Fig. 1). The choice of these particular systems for numerical simulations was motivated by our extensive previous experimental work with these materials, which enabled us to check results of the numerical modeling against various experimentally observed trends in time-resolved photoluminescence (PL), photoconductivity, and charge carrier mobility. We quantified contributions of multiple pathways of charge photogeneration to ns time-scale photocurrent which include fast formation of spatially separated charge carriers, slow charge carrier photogeneration via Frenkel exciton (FE) dissociation, and in D/A composites, charge photogeneration via CT exciton dissociation. Additionally, we obtained parameters pertaining to subsequent transport of photoexcited charge carriers such as charge carrier mobilities, charge trapping, and recombination properties.

II. EXPERIMENTAL

Details of sample preparation and experimental set up used in measurements of ns time-scale time-resolved photocurrent can be found in a previous paper. Briefly, either pristine ADT-TES-F films or composite films containing 98 wt. % of ADT-TES-F donor and 2 wt. % of acceptor molecules were drop cast from toluene solutions onto glass substrates patterned with interdigitated Cr/Au electrodes with a L = 25 μm gap between the electrodes. This method yielded polycrystalline films, as confirmed by x-ray diffraction. The HOMO (LUMO) energies were 5.35 (3.05) eV for ADT-TES-F, 5.55 (3.6) eV for Pn-TIPS-F8, and 6.1 (3.7) eV for PCBM. The low concentration of acceptor molecules in the D/A composites was chosen to minimize the disruption of film crystallinity and focus on processes at and due to heterojunctions, while neglecting effects of acceptor aggregation and acceptor domain formation. Voltage was applied to the samples, and dark current was measured as a function of voltage using a Keithley 237 source-measure unit. The average applied electric field E was calculated as E = V/L, and the studied range of electric fields was 20–80 kV/cm. For the transient photocurrent measurements, the samples were excited with a 355 nm (~3.49 eV), 0.18 μJ/cm², 500 ps pulsed laser beam (cavity Q-switched frequency-tripled Nd:YAG laser, 44.6 kHz, from Nanolase, Inc.). The transient photocurrent was measured using a 50 GHz digital sampling oscilloscope (DSO) (C88200/Tek80E01) with a broadband amplifier (Centellax UAOL65VM). The time resolution of the system was ~0.6 ns, limited by the laser pulse width and jitter. For comparison with simulated currents, both dark current and transient photocurrent values were converted to corresponding current densities, assuming an active transport channel depth of d = 1 μm, based on an average thickness of our films.

III. THEORY

A considerable recent effort was directed towards numerical modeling of the photocurrent in organic solar cells. Most approaches have focused either on solving a fully space-dependent set of drift-diffusion equations or on Monte Carlo simulations of photoexcited charge carriers.

For our device geometry, a system of drift-diffusion equations is excessively computationally expensive to solve, since the channel length of the device is 25 μm, more than two orders of magnitude larger than that in typical solar cells. Instead, we assumed that the electric field and carrier densities can be averaged to a uniform spatial distribution and that under our experimental conditions drift current dominates over diffusion. The former assumption is supported by our previous observation of weak dependence of the amplitudes and dynamics of fast transient photocurrents on the position of the localized excitation in the gap between the electrodes. The latter consideration is similar to that applied to modeling cw photocurrent dynamics in, for example, photorefractive polymer devices and to modeling transient photocurrent decays in polymeric devices with channel lengths on the order of tens of microns.

A. Charge photogeneration

Our previous studies of pristine ADT films revealed fast charge carrier photogeneration (inferred from sub-30 ps
photocurrent rise times under 100 fs pulsed excitation, limited by the time resolution of the DSO detection), high-cw photocconductivity, and relatively strong PL, which indicates existence of several relaxation pathways following the photoexcitation. In particular, fast charge carrier photogeneration observed upon excitation of films with a pulsed light with a photon energy considerably above the ADT-TES-F HOMO-LUMO gap of 2.3 eV (such as with a 3.49 eV light used here) could be due to a direct band-to-band excitation of charge carriers or due to hot exciton dissociation at ps or sub-ps time scales. Regardless of the exact origin of the carriers created on fast (ps or sub-ps) time scales, in our further discussion, we will refer to such carriers as “spatially separated carriers” (SSC) (charge generation path 1 in Fig. 2). Additionally, a large percentage of the initial excitation relaxes into a FE which could dissociate under applied electric fields creating charge carriers contributing to the photocurrent at time scales of the exciton lifetime (path 2 in Fig. 2). In the D/A composite films, our previous work suggests the existence of yet additional channel (path 3 in Fig. 2). In the D/A composite films, our previous studies of the exciton lifetime indicate existence of several relaxation pathways following the photoexcitation. In particular, fast charge carrier photogeneration due to dissociation of the CT exciton created by a Coulombically bound hole on the donor molecule and an electron on the acceptor molecule (path 4 in Fig. 2). Efficiency of this channel depends on the electron/pair separation in the FE or CT exciton.

C. Model

Given the considerations above, the resultant equations are as follows:

\begin{align}
\frac{dn_f}{dt} &= \xi_{SSC}(E(t))G(t) + k_{diss,FE}X_{FE} - \gamma n_f p_f \\
&\quad - B_n(N_n - n_f)n_f - B_{n,p}n_f p_f \\
&\quad [+k_{diss,CT}X_{CT}], \\
\frac{dn_t}{dt} &= B_p(N_p - n_t)n_f - B_{p,n}n_f p_t, \\
\frac{dp_f}{dt} &= \xi_{SSC}(E(t))G(t) + k_{diss,FE}X_{FE} + B_p p_t - \gamma n_f p_f \\
&\quad - B_p(N_p - p_f)p_f - B_{p,n}p_f p_t \\
&\quad [+k_{diss,CT}X_{CT}], \\
\frac{dp_t}{dt} &= B_p(N_p - p_f)p_f - B_{p,n}n_f p_t - B_{p,n}p_f p_t, \\
\frac{dX_{FE(CT)}}{dt} &= \xi_{FE(CT)}(E(t))G(t) - k_{diss,FE(CT)}X_{FE(CT)} \\
&\quad - k_{r,FE(CT)}X_{FE(CT)}, \\
\gamma &= e(\mu_n + \mu_p)/(\varepsilon_0 e_r), \\
k_{diss,FE(CT)}(E,T) &= \frac{3\gamma J_2(2\sqrt{2}b)}{4\pi a_{FE(CT)}^2} \exp\left(-\frac{E_{B,FE(CT)}}{k_B T}\right), \\
b &= \left(\frac{e^3}{\varepsilon_0}\right) / \left(8\pi a_{FE(CT)}^2 k_B T\right)^2, \\
J &= eE\left(\mu_n(E)n_f + \mu_p(E)p_f\right), \\
\mu_n(p)(E) &= \mu_{n(p)}(E) e^{\left(\gamma_{n(p)}\sqrt{E}\right)},
\end{align}

FIG. 2. Schematic of the different relaxation pathways upon photoexcitation, with pathways 1, 2, and 4 leading to charge generation described by the model of Eqs. (1)-(12). (1) Fast formation of SSC; (2) Formation of a FE in ADT-TES-F, which can dissociate at ns-time-scales to free charge carriers; (3) Formation of a relaxed exciton that does not yield free charge carriers at ns-time-scales and instead recombines to the ground state either radiatively or non-radiatively; (4) CT exciton in D/A composites that can dissociate to free carriers during its lifetime. Parameters $\xi_{SSC,FE(CT)}$ represent fractions of the absorbed photon density corresponding to the SSC, FE, or CT pathways, and $\mu_{n(p)}(E)$ is an electron-pair separation in the FE or CT exciton.
where \( t \) is the time, \( e \) is the fundamental charge, \( \epsilon_0 \) is the permittivity of free space, and \( \epsilon_r \) is the relative permittivity of the film (taken to be 3). Variables \( p(n)_f \) correspond to free hole (electron) density, \( p(n) \) is the trapped hole (electron) density, \( X_{FE}(X_{CT}) \) are exciton densities for the FE (CT exciton), \( J \) is the total current density, \( E \) is applied electric field, \( G(t) \) is the photoexcitation rate described below (Eq. (12)), and \( \xi_{SSC(FE)(CT)} \) are fractions of the photoexcitation that result in charge photogeneration via the SSC pathway and in the FE and CT exciton formation (paths 1, 2, and 4, respectively, in Fig. 2). \( k_{diss,FE} \) \( (k_{diss,CT}) \) are dissociation rates for the FE (CT exciton), and \( k_r,FE \) \( (k_r,CT) \) are recombination rates for the FE (CT exciton). \( E_{B,FE} \) \( (E_{B,CT}) \) is the binding energy of the FE (CT exciton) given by \( E_{B,FE(CT)} = e^2/(4\pi\epsilon_0\epsilon_e\alpha_{FE(CT)}), \) where \( \alpha_{FE} \) \( (\alpha_{CT}) \) is the initial separation between charge carriers for the FE (CT exciton).

Equations (1) and (3) are the coupled drift equations for hole and electron densities, with multiple charge generation paths as described above, charge trapping, and recombination including bimolecular recombination of free carriers to the ground state with the Langevin rate constant of Eq. (6). Bimolecular recombination with a formation of the FE or CT exciton was also considered, but produced a negligible effect on the photocurrent dynamics and was omitted. Equations (2) and (4) describe the trapping, trap assisted recombination, and hole detrapping of carriers, governed by their respective rates. Equation (5) describes the dynamics of the dissociation and recombination of FEs and, in D/A composites, CT excitons. The dissociation rate of both FEs and CT excitons is given by Eq. (7), following the Onsager-Braun formalism. \( \mu_{p0}(\mu_{n0}) \) \( \gamma_p(\gamma_n) \) are Poole-Frenkel model parameters characterizing zero-field mobility and electric field dependence of mobility for holes (electrons).

Commonly used models of exciton dissociation, such as the Onsager-Braun model, consider the rate of dissociation \( k_{diss,} \) electric field dependent, whereas the primary yield of geminate pair formation (\( \xi_{FE} \)) is typically assumed to be electric field independent; this assumption has been challenged in several studies. We found that our data are more consistent with an electric field-dependent competition among pathways 1, 2, and, in composites, 4 of charge carrier photogeneration, which suggests field dependent parameters \( \xi_{SSC}, \xi_{FE}, \) and \( \xi_{CT} \). Since the analytical function describing such competition is not known, in order to extract quantitative information about relative contributions of these different charge generation pathways to the photocurrent at various applied electric fields, we used the simplest possible linear model for the electric field dependence of these parameters, specifically

\[
\xi_{SSC(FE)(CT)} = \xi_{SSC(FE)(CT)}^{(0)} + \gamma_{SSC(FE)(CT)} E, \tag{11}
\]

where the parameters \( \xi_{SSC(FE)(CT)}^{(0)} \) \( \gamma_{SSC(FE)(CT)} \) were taken to be constant over our range of electric fields. We found that this assumption worked well for pristine ADT-TES-F and ADT-TES-F/Pn-TIPS-F8 films up to electric fields of at least 80 kV/cm; however, in ADT-TES-F/PCBM films, the assumption started to break down at about 60 kV/cm (Sec. IV B).

The illumination profile of our films on interdigitated electrodes is taken to be uniform over the device. We calculated the generation rate \( G(t) \) by first assuming a perfect Gaussian laser pulse with a full width at half maximum (FWHM) of \( \tau = 500 \text{ ps} \), representative of the laser pulse used in our experiments, and then multiplying it by the density of absorbed photons \( N_{ph} \), which in our experiments is \( 2.9 \times 10^{15} \text{ cm}^{-3} \). In particular,

\[
G(t) = N_{ph} \frac{2\sqrt{\ln 2}}{\pi^{3/2}} \exp \left( -4 \ln 2 \frac{(\tau - t_{FWTM}/2)^2}{\tau^2} \right), \tag{12}
\]

where \( t_{FWTM} \) is the full width at a tenth of the maximum of the Gaussian pulse and so \( G(t = 0) = 0.1G_{\text{max}}, \) where \( G_{\text{max}} \) is the photon density at the laser pulse maximum. The constants ensure that the pulse is normalized such that \( \int_0^\infty G(t)dt = N_{ph} \). For computational purposes, the infinite integration limits were replaced by those that correspond to the duration of the simulated transient photocurrent, 0 to 20 ns.

Based on non-negligible dark currents in our films, due mostly to efficient hole injection from Au electrodes, we assumed that before the photoexcitation of the film there exists a certain density of free and trapped charge carriers that cannot be neglected. We extracted average carrier densities from dark current values as described in detail in the supplemental material, and used them as initial conditions for corresponding densities in our simulations of transient photocurrents. Briefly, for boundary conditions, we have assumed thermionic injection with image charge effects. The injection barriers for holes and electrons, \( \phi_B^0 \) \( \phi_h^0 \) \( \phi_e^0 \) \( \phi_p^0 \) \( \phi_n^0 \) \( \phi_f^0 \), respectively, were taken to be 0.25 eV and 2.05 eV, calculated from the HOMO and LUMO levels of ADT-TES-F and the work function of Au (5.1 eV). We then assumed that before the laser pulse excitation, the carrier densities have reached a steady state, so that \( d\rho(n)/dt = 0 \). Additionally, the density of chargeable sites in the material is considered to be identical for electrons and holes. Under these assumptions, we obtained the following average densities at time \( t = 0 \):

\[
\rho_f^0 = J_{Dark}(E) e^{\frac{\phi_f^0}{k_BT}} \left( \frac{1}{\mu_f e^{\frac{\phi_f^0}{k_BT}} + \mu_p e^{\frac{\phi_p^0}{k_BT}}} \right), \tag{13}
\]

\[
\rho_f^0 = J_{Dark}(E) e^{\frac{\phi_f^0}{k_BT}} \left( \frac{1}{\mu_f e^{\frac{\phi_f^0}{k_BT}} + \mu_p e^{\frac{\phi_p^0}{k_BT}}} \right), \tag{14}
\]

\[
\rho_f^0 = (B_p N_{p0}\rho_f^0)/(B_{pp}\rho_f^0 + B_{pn}\rho_f^0 + B_{pp}^0), \tag{15}
\]

\[
\rho_f^0 = (B_p N_{p0}\rho_f^0)/(B_{pp}\rho_f^0 + B_{pn}\rho_f^0 + B_{pp}^0), \tag{16}
\]

where \( J_{Dark}(E) \) is the measured dark current density at the applied electric field \( E \).

The system of Eqs. (1)–(12) with initial conditions given by Eqs. (13)–(16) was solved numerically in MATLAB using the built-in ode15s function. The simulated transients were then fit to the data using the non-linear optimization package NLOPT. Details of the fitting procedure, as well
as bounds used for each parameter and their justification, can be found in the supplemental material. Briefly, the ISRES algorithm was used for gross global fitting across a large initial parameter space, and the COBYLA algorithm was used to perform fine local minimation. Both algorithms work by minimizing a user provided objective function. The objective functions used were

\[ f_1(\vec{x}) = \sum_n (J_{\text{Data}}(t_n) - J_{\text{Sim}}(t_n, \vec{x}))^2, \]  
\[ f_2(\vec{x}) = \sum_m (1 - r_m^2), \]

where \( \vec{x} \) is the vector input to the simulation function that incorporates all varied parameters of the model, \( t_n \) is the \( n \)th discrete time value, \( J_{\text{Data}}(t_n) \) is the experimentally measured total current at \( t_n \), \( J_{\text{Sim}}(t_n, \vec{x}) \) is the simulated total current at \( t_n \), and \( r_m \) is the coefficient of determination of the simulated fit for the \( m \)th applied electric field. Using these objective functions, we obtained sets of parameters that describe experimentally measured photocurrent transients at all applied electric fields in the studied range.

**IV. RESULTS**

We now describe the process of arriving at the compound model of Eqs. (1)–(5) used in simulating photocurrent transients in pristine ADT-TES-F films and ADT-TES-F-based D/A composites.

**A. Pristine ADT-TES-F films**

In modelling transient photocurrents in pristine ADT-TES-F films, we first considered a model which included only the fast SSC generation, pathway 1 in Fig. 2 (\( \zeta_{\text{FE}} = 0 \) in Eqs. (1) and (3)). An example of the best fit result for the data taken at an applied electric field of 60 kV/cm is shown as the dashed line in the inset of Fig. 3(a). The simulated transient exhibited a fast rise followed by a considerably faster initial decay than the experimental data, with no additional, slow decay component. Although this model could reproduce the fast rise and initial decay at higher applied electric fields (above 60 kV/cm), it was unable to attain good fits for the data obtained at lower applied electric fields.

The next model examined was a model that only included the charge generation pathway via FE dissociation, pathway 2 in Fig. 2 (\( \zeta_{\text{SSC}} = 0 \) in Eqs. (1) and (3)), and attempted to fit one of the experimental data sets using the objective function of Eq. (17). A sample of the best fit attained in this case for the data taken at an applied electric field of 60 kV/cm is shown in the inset to Fig. 3(a) as the dashed-dotted line. The fits revealed that the FE dissociation-only model showed a much slower photocurrent rise than the data and did not reproduce well the transition between the fast initial decay and slow decay component occurring at about 2–3 ns. This model was capable of generating better fits at lower electric fields, but the goodness-of-fit values \( r^2 \) of such fits were still relatively low, below 0.8.

Next, we combined the fast SSC generation (pathway 1) and charge generation via FE dissociation (pathway 2) into one model. The results are presented in Fig. 3(a), with the short time-scale dynamics shown in more detail in the inset. The combined model displays the best aspects of SSC-only and FE dissociation-only models, with fast photocurrent rise, a moderately fast initial decay, and a slow decay component. This model provided consistent results for the data across the entire range of applied electric fields and attained goodness-of-fit values \( r^2 \) of 0.89–0.97 depending on the electric field.

Having found a model that could fit data at any single value of the applied electric field well, we generalized the fitting algorithm to fit data taken at all values of applied electric field simultaneously. In order to weight data for all of the different applied electric fields identically, we used Eq. (18) as the objective function. The fractions of absorbed photon density that resulted in the SSC (\( \zeta_{\text{SSC}} \)) and in the formation
of the FE state (\(n_{FE}\)), as revealed by simulations (Fig. 3(a)), are shown in Figs. 4(a) and 4(b), respectively, at various applied electric fields. As the electric field increased from 40 kV/cm to 80 kV/cm, \(n_{SSC}\) increased from 0.035 to 0.081, whereas \(n_{FE}\) decreased from \(0.2\) to \(0.15\). Good fits were obtained by applying the constraint 
\[c_{SSC} = c_{FE}\] to Eq. (11), suggesting that the pathways 1 and 2 are in direct competition with each other, originating from the same photoexcited state, such as a hot exciton. The FE dissociates with the electric field-dependent dissociation rate \(k_{diss, FE}\) (Fig. 5) during its lifetime given by 
\[\frac{1}{k_{diss, FE} + k_{FE}}\] (Figs. 6 and S1). The efficiency of the exciton dissociation occurring over time scales of the exciton lifetime is given by 
\[\eta_{FE(CT)} = \frac{k_{diss, FE(CT)}}{k_{diss, FE(CT)} + k_{FE}(CT)}\] (19).

For the FE in pristine ADT-TES-F films, \(\eta_{FE}\) varies between 0.56 and 0.77 in the studied range of electric fields. This yields the fraction of absorbed photon density which contributes to the photocurrent via the FE dissociation, \(\zeta_{FE}\), of

\[\eta_{tot} = \zeta_{SSC} + \zeta_{FE}\eta_{FE}\] (20).

It increases from 0.14 to 0.20 upon an increase in the electric field from 40 kV/cm to 80 kV/cm, as shown in Fig. 7. The rest of the photexcitation, given by \(1 - \eta_{tot}\), which amounts to about 80%–86% of the absorbed photon density, depending on the applied electric field, does not contribute to charge carrier photogeneration in the time domain studied.

Table I lists values obtained from fits to experimental data for other parameters of Eqs. (1)–(12). Hole mobility, exhibiting a zero-field value of \(\mu_{0}\), is consistent with TFT and space-charge-limited current mobilities in similar films. Hole trapping and detrapping properties seem to be well described by the Miller-Abrahams model, with the attempt-to-jump rate \(\nu\) of \(3.9 \times 10^{10} \text{s}^{-1}\), comparable to that in pentacene films, and the average trap depth of 29 meV similar to that of 25 meV obtained from Arrhenius fits of experimentally measured temperature dependence of the transient photocurrent in ADT-TES-F films in a previous paper by our group. The zero-field electron mobility was lower than the hole mobility by a factor of \(6\), whereas the average electron trap density was higher than the hole trap density by a factor of \(2.5\) (Table I). Both hole and electron trap densities were on the order of \(10^{18} \text{cm}^{-3}\), similar to values reported by other groups for small-molecule organic semiconductor films.
TABLE I. Parameter values extracted from experimental data for pristine ADT-TES-F films and ADT-TES-F/Pn-TIPS-F8 and PCBM acceptors using simulation with a system of Eqs. (1)–(12). Parameter descriptions are given in the text.

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>ADT-TES-F</th>
<th>2% Pn-TIPS-F8</th>
<th>2% PCBM</th>
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<tbody>
<tr>
<td>$\mu_{0}$ (cm$^2$(V·s)$^{-1}$)</td>
<td>0.093</td>
<td>0.016</td>
<td>0.025</td>
</tr>
<tr>
<td>$\mu_{p}$ (cm$^2$(V·s)$^{-1}$)</td>
<td>0.60</td>
<td>0.51</td>
<td>0.36</td>
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<tr>
<td>$\gamma_{p}$ (cm/V)$^{1/2}$</td>
<td>$1.8 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-3}$</td>
<td>$3.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\gamma_{n}$ (cm/V)$^{1/2}$</td>
<td>$3.1 \times 10^{-4}$</td>
<td>$6.0 \times 10^{-4}$</td>
<td>$9.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\Delta$ (meV)</td>
<td>29</td>
<td>41</td>
<td>39</td>
</tr>
<tr>
<td>$N_{n}$ (cm$^{-3}$)</td>
<td>$7.1 \times 10^{18}$</td>
<td>$7.4 \times 10^{18}$</td>
<td>$8.7 \times 10^{18}$</td>
</tr>
<tr>
<td>$N_{p}$ (cm$^{-3}$)</td>
<td>$2.8 \times 10^{18}$</td>
<td>$2.2 \times 10^{18}$</td>
<td>$3.8 \times 10^{18}$</td>
</tr>
<tr>
<td>$B_{0}$ (s$^{-1}$)</td>
<td>$5.1 \times 10^{14}$</td>
<td>$8.9 \times 10^{14}$</td>
<td>$7.8 \times 10^{14}$</td>
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<tr>
<td>$B_{-}$ (s$^{-1}$)</td>
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<td>$6.9 \times 10^{10}$</td>
<td>$2.1 \times 10^{11}$</td>
</tr>
<tr>
<td>$B_{np}$ (cm$^{3}$s$^{-1}$)</td>
<td>$1.4 \times 10^{-3}$</td>
<td>$5.0 \times 10^{-3}$</td>
<td>$4.0 \times 10^{-3}$</td>
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<tr>
<td>$B_{pn}$ (cm$^{3}$s$^{-1}$)</td>
<td>$2.1 \times 10^{-5}$</td>
<td>$2.7 \times 10^{-5}$</td>
<td>$8.2 \times 10^{-7}$</td>
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<tr>
<td>$a_{\text{FE}}$ (nm)</td>
<td>1.18</td>
<td>1.18</td>
<td>1.18</td>
</tr>
<tr>
<td>$a_{\text{CT}}$ (nm)</td>
<td>...</td>
<td>1.22</td>
<td>1.77</td>
</tr>
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</table>

B. D/A composites

The model that takes into account the SSC and FE channels of carrier photogeneration produced good fits for the pristine ADT-TES-F film photocurrents, but it was unable to accurately replicate some of the more complicated dynamics of photocurrents from composites. The insets of Figs. 3(b) and 3(c) show the best results of fitting the photocurrent at 8%–12%, which is consistent with our previous observation of a strong PL emission from the ADT-TES-F/Pn-TIPS-F8 composite. It also dominated over the pathway 2 charge carrier photogeneration in the time domain studied.

Based on these considerations, to accurately reproduce the photocurrent dynamics in the composites with the Pn-TIPS-F8 and PCBM acceptors, we added the charge generation pathway 4 in Fig. 2, which proceeds via CT exciton dissociation, to the set of equations (Eq. (5)) and additional terms to Eqs. (1) and (3). To describe CT exciton dissociation, we used the Onsager-Braun model, similar to that of the FE dissociation, but with a different initial pair separation $a_{\text{CT}}$ and recombination rate $k_{\text{CT}}$. Thus, in D/A composites, there are three competing channels of charge photogeneration: the first SSC pathway, FE dissociation, and CT exciton dissociation (pathways 1, 2, and 4, respectively, in Fig. 2), with relative contribution of each pathway to the overall charge photogeneration being electric field dependent. Since the exact pathway of the CT state formation is unknown, we did not impose restrictions on the relative values of $\gamma_{\text{SSC}}$, $\gamma_{\text{FE}}$, and $\gamma_{\text{CT}}$ in Eq. (11). Following the same fitting process as described above, we fit the experimental data to the simulated photocurrent transients (Fig. 3). The addition of the CT exciton dissociation improved the goodness-of-fit ratings for the fits to the data from the composite films (Figs. 3(b) and 3(c)). The fit to the data from the composite with the PCBM acceptor at an applied electric field of 60 kV/cm was lower in quality than the fits to the data at lower electric fields due to breaking down of the assumption of Eq. (11) at higher electric fields. As in pristine ADT-TES-F films, in both D/A composites under consideration, the efficiency of fast carrier generation via the SSC pathway was below 10% (Fig. 4(a)).

In the composite with the Pn-TIPS-F8 acceptor, ~0.12 (~0.04–0.08) of the absorbed photon density $N_{ph}$ formed the charge-generating FE (CT exciton) (Fig. 4(b)). These dissociated during their lifetimes (Figs. 6 and S1) with the electric field dependent efficiency $\eta_{\text{FE}}$ ($\eta_{\text{CT}}$), calculated using Eq. (19), of 0.49–0.72 (0.17–0.35) in the studied range of electric fields. This yields a fraction of $N_{ph}$ contributing to the overall charge photogeneration via the FE (CT exciton) dissociation pathway, $\xi_{\text{FE}}\eta_{\text{FE}}$ ($\xi_{\text{CT}}\eta_{\text{CT}}$), of 0.062–0.088 (0.014–0.015). The contribution of the CT dissociation to charge carrier generation in this composite, given by $\xi_{\text{CT}}\eta_{\text{CT}}/\eta_{\text{tot}}$, is the lowest of the three contributing pathways at 8%–12%, which is consistent with our previous observation of a strong PL emission from the ADT-TES-F/Pn-TIPS-F8 CT state (exciplex), indicative of a tightly bound CT state with a relatively low dissociation rate $k_{\text{diss,CT}}$ (Fig. 5). The total fraction of the absorbed photon density which results in charge carrier photogeneration at time scales of ~20 ns, is

$$\eta_{\text{tot}} = \xi_{\text{SSC}} + \xi_{\text{FE}}\eta_{\text{FE}} + \xi_{\text{CT}}\eta_{\text{CT}}.$$  

It increases slightly, from ~0.11 to ~0.17, as the electric field increases from 40 kV/cm to 80 kV/cm (Fig. 7). The rest of the photoexcitation, given by 1 − $\eta_{\text{tot}}$, which amounts to ~83%–89% of the absorbed photons, does not contribute to charge carrier photogeneration in the time domain studied.

In the composite with the PCBM acceptor, the CT exciton formed considerably more efficiently ($\xi_{\text{CT}}$ in Fig. 4(b)) and was considerably more prone to dissociation as compared to that in the composite with the Pn-TIPS-F8 acceptor. As a result, the contribution of the CT exciton dissociation (pathway 4) into the overall charge photogeneration, $\xi_{\text{CT}}\eta_{\text{CT}}$, of 0.12–0.13 (i.e., 12%–13%) of the absorbed photon density was a factor of ~8.5 larger than that in the ADT-TES-F/Pn-TIPS-F8 composite. It also dominated over the pathway 2...
Ultrafast charge carrier photogeneration has been observed in a variety of small-molecule and polymeric organic semiconductors via ultrafast spectroscopy methods,\textsuperscript{26,77–79} Aumont switch-based techniques,\textsuperscript{39,80,81} and fast oscilloscope detection of photocurrents.\textsuperscript{33,54,82} In most cases, the efficiency of this process is at or below \( \approx 10\% \), in agreement with values of \( \xi_{\text{SSC}} \) (which dominates charge generation at fast time scales) extracted from our simulations. Many of these methods enable determination of the product of the sum of hole and electron mobilities \((\mu_{\text{hole}} + \mu_{\text{electron}})\) and of the photogeneration efficiency. In our films the \( \mu_{\text{hole}} \xi_{\text{SSC}} \) values (Fig. 4(a) and Table I) are between \( \approx 0.02 \) and \( 0.06 \) cm\(^2\)/Vs, in good agreement with experimental observations from similar films.\textsuperscript{33,54,78} However, the mechanism of achieving the SSC state at ultrafast time scales in ADT films is unknown and requires further investigation. Two main possibilities are direct band-to-band excitations\textsuperscript{26} and hot exciton dissociation,\textsuperscript{56} with the electric field dependence of the parameter \( \xi_{\text{SSC}} \) observed here more consistent with the latter process.

The simulations revealed that a FE with lifetimes on the order of 10–20 ns (Figs. 6 and S1) contributes a considerable number of charge carriers at ns time-scales through pathway 2 in Fig. 2. In the studied D/A composites, the FE lifetimes were similar to those in the pristine ADT-TES-F film (Fig. 6), which confirms that the FE state is formed on the ADT-TES-F donor. There are several possible origins of such FE states. For example, these could be dark states that are delocalized over several ADT-TES-F molecules in the ADT-TES-F H-aggregates,\textsuperscript{58} similar to those in H-aggregates of sexithiophene films.\textsuperscript{83} The pristine ADT-TES-F films and both D/A composites considered here exhibit a relatively strong PL at or below SSC (which dominates charge generation at fast time scales) extracted from our simulations. Many of these methods enable determination of the product of the sum of hole and electron mobilities \((\mu_{\text{hole}} + \mu_{\text{electron}})\) and of the photogeneration efficiency. In our films the \( \mu_{\text{hole}} \xi_{\text{SSC}} \) values (Fig. 4(a) and Table I) are between \( \approx 0.02 \) and \( 0.06 \) cm\(^2\)/Vs, in good agreement with experimental observations from similar films.\textsuperscript{33,54,78} However, the mechanism of achieving the SSC state at ultrafast time scales in ADT films is unknown and requires further investigation. Two main possibilities are direct band-to-band excitations\textsuperscript{26} and hot exciton dissociation,\textsuperscript{56} with the electric field dependence of the parameter \( \xi_{\text{SSC}} \) observed here more consistent with the latter process.

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produce charge carriers. However, since the PL lifetimes of the FE in Fig. 6 are close to PL lifetimes of isolated ADT-TES-F molecules, the alternative assignment for the FE composite (trapped electrons and free holes in the ADT-TES-F/PCBM ADT-TES-F films. Based on our simulation results, this is composite with the PCBM acceptor as compared to pristine tion, are considerably higher (by a factor of obtained by integrating transient photocurrents over this time
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the amount of mobile charge over the period of 1
l 
charge carrier photogeneration, as well as extract parameters enabled us to quantify contributions of multiple pathways to the photocurrent.27,84 Our simulations confirm the Pn-TIPS-F8, both of which factors have been shown to enhance the photocurrent.27,84 Indeed, low contribution of the CT states to the photocurrent in this composite is consistent with a highly emissive tightly bound exciplex, in agreement with experiments.27 The CT state in the composite with the PCBM acceptor was found to exhibit considerably lower lifetimes (Figs. 6 and S1) than those of the ADT-TES-F FE and the CT in the composite with the Pn-TIPS-F8 acceptor. Additionally, it was more dissociative than either of these excitons (Fig. 5), which is consistent with a larger LUMO offset between ADT-TES-F and PCBM and larger D/A separation due to the size of the PCBM molecule as compared to Pn-TIPS-F8, both of which factors have been shown to enhance the photocurrent.27,84 Our simulations confirm the latter statement, yielding the initial charge pair separation $a_{CT}$ of 1.77 nm in the ADT-TES-F/PCBM composite, as compared to that of 1.22 nm in the ADT-TES-F/Pn-TIPS-F8 composite.

The total amount of charge generated at ns time-scales, 0.1–0.25 of absorbed photon density (Fig. 7), only differs by a factor of ~2 in all three systems under study, with the highest in the composite with the PCBM acceptor followed by pristine ADT-TES-F film and the composite with the Pn-TIPS-F8 acceptor, consistent with our previous observations.27 However, our previous studies also established that the amount of mobile charge over the period of 1 μs, obtained by integrating transient photocurrents over this time period, as well as photocurrents obtained under cw illumination, are considerably higher (by a factor of ~6–10) in the composite with the PCBM acceptor as compared to pristine ADT-TES-F films. Based on our simulation results, this is due to a considerably lower rate of recombination between trapped electrons and free holes in the ADT-TES-F/PCBM composite ($B_{ph}$, in Table I and Fig. S2), which results in a significantly slower decay of the photocurrent in this composite, and thus, higher charge retention, as compared to that in pristine ADT-TES-F films.

**VI. CONCLUSIONS**

We presented a model based on drift conduction which enabled us to quantify contributions of multiple pathways to charge carrier photogeneration, as well as extract parameters that characterize charge transport in pristine organic films and organic D/A composites from transient photocurrents. In pristine ADT-TES-F films, simulations revealed two competing charge photogeneration pathways: fast charge generation, on a ps or sub-ps time scale, with efficiencies below 10%, and slow, on the time scale of tens of nanoseconds, with efficiencies of about 11%–12%, at the applied electric fields of 40–80 kV/cm. The relative contribution of these pathways to the photocurrent was electric field dependent, with the contribution of the fast process increasing with applied electric field. However, the total charge photogeneration efficiency was weakly electric field dependent exhibiting values of 14%–20% of the absorbed photon density. The remaining 80%–86% of the photoexcitation did not contribute to charge carrier generation at these time scales. In ADT-TES-F-based D/A composites, an additional pathway of charge photogeneration that proceeds via CT exciton dissociation contributed to the total charge photogeneration. In the composite with the 2 wt.% Pn-TIPS-F8 acceptor, which exhibits strong exciplex emission from a tightly bound D/A CT exciton, the contribution of the CT state to charge generation was small, ~8%–12% of the total number of photogenerated charge carriers, dependent on the electric field. In contrast, in the composite with 2 wt.% PCBM acceptor, the CT state contributed about a half of all photogenerated charge carriers. In both D/A composites, the charge carrier mobilities were reduced and trap densities and average trap depths were increased, as compared to a pristine ADT-TES-F donor film. A considerably slower recombination of free holes with trapped electrons was found in the composite with the PCBM acceptor, which led to slower decays of the transient photocurrent and considerably higher charge retention, as compared to a pristine ADT-TES-F donor film and the composite with the Pn-TIPS-F8 acceptor.

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