Control of Geminate Recombination by the Material Composition and Processing Conditions in Novel Polymer:Non-Fullerene Acceptor Photovoltaic Devices

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Abstract: Herein, we report on the charge dynamics of photovoltaic devices based on two novel small-molecule non-fullerene acceptors featuring a central ketone unit. Using ultrafast near infrared spectroscopy with optical and photocurrent detection methods, we identify one of the key loss channels in the devices as geminate recombination (GR) of interfacial charge transfer states (CTSs). We find that the magnitude of GR is highly sensitive to the choice of solvent and annealing conditions. Interestingly, regardless of these processing conditions, the same lifetime for GR (~ 130 ps) is obtained by both detection methods upon decomposing the complex broadband transient optical spectra, suggesting this timescale is inherent and independent of morphology. Our result suggests that the CTSs are mostly strongly bound, and that charge generation from these states is highly inefficient. We further rationalize our results by considering the impact of the processing on the morphology of the mixed donor and acceptor domains, and discuss the potential consequences of the early charge dynamics on the performance of emerging non-fullerene photovoltaic devices. Our results demonstrate that careful choice of processing conditions enables enhanced exciton harvesting and suppression of GR by more than 3 orders of magnitude.

Introduction

The past several years have witnessed a rapid improvement to the power conversion efficiency (PCE) of single-junction organic solar cells (OSCs), with current record efficiencies in excess of 13%.¹ Much of this progress is due to the continuing development of non-fullerene small-molecule acceptors (NF-SMA).^{2–20} Compared with the fullerene-based solar cells, NF OSCs exhibit superior thermo- and photo- stability, more tunable energy levels, higher electron mobility, and stronger absorption cross sections.^{2,21,22} The impressive progress in the single-junction efficiencies has also motivated research on more complex materials systems, such as ternary blends reaching over 12% PCE,²³ or semi-transparent and efficient (~10%) devices for tandem applications.²⁴ This progress is accompanied by the overall improvement of the efficiency-stability-cost combined value.²² All these advances might allow flexible and tunable OSCs to be competitive with silicon and perovskite solar cells for future commercialization.

Relatively speaking, the photophysics of fullerene-based OSCs is well-understood.²⁵ These OSCs typically employ a single active layer comprising a bulk-heterojunction (BHJ) architecture^{26,27}: a nanoscale mixture of the electron-donor (D) and -acceptor (A) components. This structure provides a large interfacial donor-acceptor (D-A) surface area for the dissociation of photo-generated excitons, allowing holes and electrons to transfer to the D and A, respectively. The resultant charge pair at the interface is defined as the “charge transfer state” (CTS) due to the Coulomb interaction between electron and hole. Some states overcome this interaction directly and separate into free charges, while the others thermalize and form localized CTSs. Without special notice, CTSs mentioned below refer to localized CTSs. From this localized state, the electron-hole pair experiences relaxation to the ground state, usually by geminate recombination (GR). Another loss channel comes from bimolecular recombination (BR). In most polymer:fullerene blends, the large share of long-range charge separation is shown to occur directly after exciton dissociation at the ultrafast timescale. This is probably facilitated by the strong coupling between the exciton and charge-separated states and

by the strong coupling with different fullerene molecules.^{28,29} This coupling and electron delocalization due to fullerene aggregation was suggested to play a critical role in promoting photocurrent generation.^{28–31}

In contrast to the research on fullerene-based systems, a detailed photophysical understanding of NF OSCs still lags behind the continuing advancements in their efficiency.^{32–39} The high efficiency of many NF-SMA solar cells arises from two aspects: 1) tunable energy levels, and 2) strong and complementary light absorbing abilities. Combining these two features together may result in different charge generation mechanisms than those observed for fullerene-based systems. In contrast to sub-ps charge generation in fullerene-based cells, slow but efficient charge transfer^{4,34} was observed in NF OSCs when material combinations with a lower driving energy were used. Considering the high external quantum efficiency achieved in high-performance NF OSCs, GR should not act as a limiting loss mechanism, and CTSs should be able to efficiently separate into free carriers, being collected before recombination.

For efficient NF-SMAs, the most promising materials seem to be based on A-D-A ladder-type structures. For instance, A-D-A molecules employing indacenodithiophene (IDT)⁴⁰ as the central building block, with 2-(3-oxo-2,3-dihydroinden-1-ylidene)-malononitrile (INCN) as the capping groups, has effectively pushed the efficiency of NF OSCs above 10% and kept the highest efficiency above 13%.¹ Some other central units, such as benzodi(cyclopentadithiophene) (BDT)³, previously quite popular in donor design,⁴¹ and thiophene-thieno[3,2-b]thiophene-thiophene,⁴² were shown to be excellent candidates with above 10% efficiency. There is broad interest within the community to explore further building blocks for A-D-A molecules. In particular, low-bandgap NF molecules ($E_g < 1.5$ eV) with extended absorption into the near-infrared (NIR) region give better device performance and are receiving increased interest.^{9,42} In our previous work, we have synthesized two new NF-SMAs. Both molecules contain a ketone-based central building block, 9-fluoronone (FN) or 9,10-anthraquinone (ANQ), and are both capped with diketopyrrolopyrrole (DPP) groups. However,

unexpectedly, devices based on these new molecules gave a low PCE of ~1%. Understanding which step in the charge generation processes limits the device efficiency might offer new insight into the photophysics of NF OSCs, and help to further the device optimization.

In this paper, we studied the charge dynamics of two A-D-A type NF-SMAs with poly(3-hexylthiophene-2,5-diyl) (P3HT) as the donor. By using ultrafast NIR spectroscopy methods, namely pump-push photocurrent (PPP) spectroscopy, we identified GR as the main loss channel in a batch of devices made with different processing (varying solvent and annealing) conditions. We also performed transient absorption spectroscopy (TAS) and global data analysis to build a comprehensive photophysical picture for the dynamics of excitons, CTSs and free carriers. Combining with the morphological analysis, we are able to rationalize our results and discuss the implications for the optimization of emerging NF OSCs.

Methods

Materials and Devices. P3HT (Mw = 60,000 Da) was purchased from Rieke Metals, and 9-fluorenone and 9,10-anthraquinone end-capped with diketopyrrolopyrrole (DPP-ANQ-DPP and DPP-FN-DPP) were synthesized according to methods described before.⁴³ Thin films were prepared from 1 cm × 1 cm glass substrates, which were sequentially cleaned by sonication in acetone and 2-propanol for 10 min each followed by another 10-min UV-ozone treatment. The substrates were then moved into a glovebox under nitrogen atmosphere for active layer deposition. The optimum blend weight ratio was 2:1 for P3HT:DPP-FN-DPP with spin speed of 3000 revolutions per minute (RPM) and 1:2 for P3HT:DPP-ANQ-DPP with spin speed of 1000 RPM. Immediately after deposition, half of these samples were annealed at 120 °C for 5 min. Devices were made with a ITO/ZnO/PEIE/active layer/MoO_x/Ag structure. The detailed device fabrication description is included in the SI.

Current Density-Voltage Measurements. Current density-voltage curves of the solar cells were recorded by a Keithley 2635 source meter under illumination of a solar simulator (SS50AAA, Photo Emission Tech). The intensity of the simulated sunlight (100 mW cm^{-2}) was calibrated with a standard silicon reference cell and a KG3 filter. The external quantum efficiency (EQE) spectrum was measured by an Oriel Cornerstone 130 monochromator.

Pump-Push Photocurrent Spectroscopy. Ultrafast 100-fs pulses at $\sim 800 \text{ nm}$ with power of 3.5 W were generated from a regenerative 1 kHz Ti:Sapphire amplifier system (Spectra Physics, Solstice). A portion of this power was taken to produce visible pump pulses (with the energy of $\sim 1 \text{ }\mu\text{J}$ per pulse) at $\sim 540 \text{ nm}$ through a non-linear optical amplifier (NOPA), while another portion was used to pump an optical parametric amplifier (TOPAS, Light Conversion), generating the near-infrared push light at $\sim 2 \text{ }\mu\text{m}$. Pump and push pulses were focused onto the same spot ($\sim 1 \text{ mm}^2$) on the short-circuited device. The reference photocurrent (J), generated with the pump pulses, was recorded by a lock-in amplifier (SRS 830, Stanford Research System). The push pulses were modulated by a mechanical chopper (MC2000, Thorlabs) at $\sim 370 \text{ Hz}$. This push-induced effect was detected by the synchronized lock-in amplifier and was recorded as dJ .

Transient Absorption Spectroscopy. The transient absorption experiment was performed with a commercial transient absorption spectrometer (HELIOS, Ultrafast Systems). Ultrafast pulses at $\sim 800 \text{ nm}$ from a regenerative Ti:Sapphire amplifier system (Spectra Physics, Solstice) were sent into TOPAS-Prime (Light Conversion) to generate tunable pump pulses ($\sim 355\text{-}2600 \text{ nm}$), while another portion was sent into a delay stage, followed by generation of broadband probe pulses ($\sim 800\text{-}1400 \text{ nm}$) using a substrate made of yttrium aluminum garnet. Part of the probe light was split and used as the reference to reduce pulse amplitude fluctuation. Both probe and reference beams were sent into their corresponding fibers and measured with spectrometers. The beam size of pump and probe pulses were estimated to be $\sim 0.5 \text{ mm}^2$ and the time resolution of pulses to be $\sim 200 \text{ fs}$.

Global analysis of TA data. Genetic algorithm is a global fitting method to decompose the overlapping spectral signatures of various spectral species and obtain their relevant kinetics. The detailed description can be found elsewhere.⁴⁴ In short, a large number of random spectra are generated and selected to form later generations according to their fitness compared to the original spectra. For a certain solution, the fitness is evaluated as the inverse sum of squared residual and an additional penalty is added for non-physical results. The selected spectra are then modified by mutating with each other to avoid local minima, similar to the natural evolution process. This flexible method allows for avoiding pure mathematical solutions to a large extent and obtains physically reasonable solutions, which usually performs better than singular value decomposition.

Results and Discussion

Figure 1. (a,b) Chemical structures and energy levels of the donor material (P3HT) and two novel non-fullerene acceptor molecules, DPP-ANQ-DPP and DPP-FN-DPP. (c) Absorption spectra of the pristine non-fullerene acceptors and the annealed blends.

Materials and Devices Fig. 1a shows the chemical structures of the novel NF-SMAs, DPP-FN-DPP and DPP-ANQ-DPP, respectively. These molecules incorporate either 9-fluorenone or 9,10-anthraquinone as the core moieties, and are both capped with diketopyrrolopyrrole end groups. The

energy levels of highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO) , taken from our previous study (ref 43), are shown in **Fig. 1b**. **Fig. 1c** presents the absorption spectra of the pure films. The small peak at around 680 nm probably comes from π - π stacking of the small molecules.⁴⁵ Because the absorption spectra of these molecules are different to that of P3HT, the donor and acceptor components can be selectively excited, as shown later. In our experiment, the excitation wavelength is $\sim$ 700 nm, except where specifically stated.

To better control the experimental conditions, we measured 8 different devices by varying acceptors (DPP-FN-DPP and DPP-ANQ-DPP), processing conditions (as cast and annealing) and solvent types (dichlorobenzene, DCB and chloroform, CF). The device characteristics are summarized in **Table S1** and **Table S2**. We believe, dissimilar optimal concentrations (2:1 for P3HT:DPP-FN-DPP and 1:2 for P3HT:DPP-ANQ-DPP) might be related to the morphological difference between fluorenone and anthraquinone units in the acceptor when forming solid-state stacking in the film. In our previous work, device efficiency was doubled after thermal annealing processing for P3HT:DPP-FN-DPP (from 0.58% to 1.2%) and P3HT: DPP-ANQ-DPP (from 0.46% to 0.7%) devices.⁴³ As shown by the morphological study, these enhancements in efficiency are due to the improved crystallinity of both P3HT and NF-SMA phases, increasing the electron and hole mobilities. However, the detailed photophysics behind these changes in efficiency, and more importantly, the identity of the efficiency-limiting photophysical process, are still not completely clear.

Pump-Push Photocurrent Spectroscopy In order to further understand the difference in charge dynamics in these two novel NF-SMAs, we perform ultrafast pump-push photocurrent spectroscopy and TAS on the relevant films and devices.

Figure 2. PPP responses for devices with CF (a) and DCB (b) as the solvent. (c) Scatter map showing the inverse relationship between $\Delta J/J$ and photocurrent for devices with different processing conditions. Solid fitting lines in (a) and (b) are multi-exponential guides to the eye, and the straight dash line in (c) is guide to the eye as well.

Fig. 2a and **Fig. 2b** illustrate the kinetics from PPP spectroscopy. All eight curves are divided into two panels (a) and (b), considering the large variation in amplitude. This amplitude variation is correlated with the solvent type used for sample preparation, CF and DCB. . In PPP experiments, the ratio between the push-induced current dJ and pump-induced reference current J is proportional to the ratio between of the ratio between bound and free carriers.⁴⁶ Importantly, dJ/J does not depend on charge collection efficiency or bimolecular recombination. As the number of free (collected)

carriers does not change at ns time scale, the evolution of dJ/J in time is proportional to the number of bound carriers and reflects their GR to the ground state.⁴⁷ The maximal amplitude, dJ_{max}/J , therefore characterizes the overall efficiency of long-range charge separation; less GR means better charge separation, and hence a smaller dJ_{max}/J value is observed. In **Fig. 2c**, a larger photocurrent in x-axis correlates with an exponentially smaller dJ_{max}/J in y-axis, which suggests that the device performance is mainly limited by GR. Even though GR in some devices is small, there are still other processes limiting the device efficiency, mainly bimolecular recombination. This is seen as a low FF in Table S1, and does not change much when varying processing methods. However, to further study BR is out of this paper's scope. We note that due to the non-zero background signal, we take the signal change just after time zero and before zero as $\Delta J/J$ for further comparison.

Table S1 lists J and $\Delta J/J$ of the eight devices under study. In general, thermal annealing reduces $\Delta J/J$, which indicates that GR can be suppressed by optimizing the morphology. However, this processing does not necessarily result in a higher photocurrent, for example, between Sample **5** and **7**. This suggests that even though GR is suppressed, the following charge collection and overall device performance might be hindered due to morphological issues, for instance degradation of the bicontinuous D-A network. Another observation is that the solvent used for device fabrication has a major effect on GR. When DCB is used as the solvent (Samples **1-4**), the photocurrent is above 40 nA and $\Delta J/J$ is less than 10^{-3} . When CF is used as the solvent (Sample **5-8**), the photocurrent is smaller than 20 nA and $\Delta J/J$ is larger than 2×10^{-3} . The solvent is known to be critical for the formation of a favorable blend morphology. Further work towards optimizing the annealing conditions in order to maintain a bicontinuous network⁴⁸ might further improve the device efficiency of DPP-FN-DPP and DPP-ANQ-DPP devices.

To compare these three conditions more clearly, we constructed **Table S4** which shows how GR is sensitive to each variable by fixing the other two conditions. From this table, it is quite clear that the

solvent type is the most influential parameter, which agrees with our earlier analysis. Interestingly, it seems that there is no fundamental difference in the level of GR between the two NF-SMAs.

Although the type of NF-SMA is not as influential as other two parameters, the analysis reveals that the FN and ANQ moieties behave differently. In the as-cast film, DPP-ANQ-DPP hinders P3HT crystallization while DPP-FN-DPP does not.⁴³ This results in a very low photocurrent (0.5 nA) and extremely high $\Delta J/J$ for Sample 8 in **Table S3**. The $\Delta J/J$ as large as 0.37 is the maximal number we have measured, which shows a tremendous amount of bound CTSs at the interface failing to escape GR.

Transient Absorption Spectroscopy To further understand the early charge generation and recombination dynamics, we performed TAS experiments on P3HT:DPP-ANQ-DPP films.

Figure 3. Broadband transient absorption spectroscopy for P3HT:DPP-ANQ-DPP films. (a,b) Spectral slices spanning from 900 nm to 1350 nm; (c,d) Selected kinetics showing the decay of mainly

excitonic and polaronic contributions. The grey reference line shows the dynamics of recombination of bound CT states in the as-cast film. The arrow in (d) indicates that curves are normalized at 5 ps.

Figure 3 shows the spectra and kinetics obtained from broadband TAS comparing the same material blend (P3HT:DPP-ANQ-DPP) with different processing conditions. The broadband probe (900-1350 nm) can result in the photo-induced absorption (PIA) of different species, which gives a comprehensive knowledge of the studied material system. To understand the complex spectra with overlapping PIA responses, we first assigned different spectral contributions to the relevant species. In **Fig. 3a** at very early time (within 500 fs), we assigned a Gaussian-like peak around 1250 nm to the acceptor exciton PIA. This exciton signal decays and the spectrum evolves into another peak at 950 nm after ~10 ps, which we assigned to the exciton dissociation and formation of CTSs. Later (around 5 ns), a different spectrum is seen with a peak at ~1020 nm which we assign to free charges. In **Fig. 3b**, the exciton signature even at 0.5 ps is much weaker compared with the same line in **Fig. 3a**, which suggests an ultrafast exciton dissociation within several hundred fs. Accompanied with the decrease of exciton signal, there is an obvious appearance of CTS signature. Assuming the same absorption coefficient in both films, from the amplitude of CTS signal, the number of CTSs in annealed film is around half of that in as-cast film, indicating direct charge generation is enhanced through bypassing CTS formation. This is similar to previous studies on P3HT:fullerene blends.⁴⁹

In **Fig. 3c** and **Fig. 3d**, we selected two representative wavelengths at around 900 nm and 1300 nm regions to retrieve the kinetics of excited states. In **Fig. 3d**, an ultrafast decay (several hundred femtoseconds) of the exciton signal is observed, while after several picoseconds, the signal is dominated by CTS signal across the whole spectrum. The decay of TAS signal associated with CTSs matches very well the decay of pump-push response measured in the same devices (grey line). This strongly supports that this species identified in TAS are related with local (bound) CTSs. We emphasize that PPP spectroscopy only measures the bound CTSs that do not contribute to the photocurrent, while TAS measures all the localized CTSs. The good match between both techniques

suggests that the thermal activation of localized CTs to free charges, sometimes called ‘cold’ charge separation pathway, is minimal. These CTs are generated after the exciton dissociation and decay through GR to ground states, which is a dominant loss channel. However, in **Fig. 3c**, the grey reference line does not fully overlap with the kinetics around 900 nm. This probably comes from the comparable population of multiple species and spectral overlap.

Figure 4. GA decomposition of the broadband pump probe spectra. (a) Spectra of excitons and free charges are fixed and extracted from 0.4-0.5 ps and 5-5.5 ns, and the spectra of CTs is obtained from GA algorithm. (b) The respective kinetics. The red line is the power law fit and the blue and black lines are the single exponential fitting.

Global Analysis of TA data To separate the overlapping PIA signals measured in **Fig. 3a**, we used a global analysis technique based on a genetic algorithm (GA) which imitates the natural selection process to select the best fitting solution. **Figure 4** shows the deconvoluted spectra and kinetics. The spectrum at 0.4-0.5 ps was fixed as the ‘pure’ exciton signal, and the long-lived signal at 5-5.5 ns was fixed for free charges; CTs should have negligible contribution at these timescales. The absorption by CTs peaks around 940 nm, while free charges absorb mostly at ~1000 nm. This supports our previous observation that two species except excitons are present in the spectra, and that CTs and free charges might exhibit different absorption signatures. The difference might be caused by the local D-A morphology. The decay of excitons in **Fig. 4b** follows a power-law trend, which might be related to large domains for exciton diffusion before reaching the interface for charge transfer. The rising rate for CTs ~2 ps correlates with the decay of excitons. The decay rate of CTs after 20 ps is

133 ± 6 ps, which agrees well the decay rate of 125 ± 1 ps obtained from the red line in **Fig. 3d**. The component presented in the bottom panel shows very slow increase, which we assign to the generation of free charges. This signal does not change much after 500 ps. probably as BR does not happen yet due to a low concentration and/or mobility of free carriers.

Figure 5. Diagram of the relevant charge dynamics of the P3HT:DPP-ANQ-DPP blends. After annealing processing together with solvent change, slower charge generation rate and more efficient charge separation result in better device performance. The energy level of singlet state was estimated from HOMO-LUMO gap for the acceptor (~1.7 eV) and CT state from the diagonal gap between acceptor and donor (~1.3 eV).

Photophysical Model

Figure 5 presents the photophysical model summarizing the observation from both PPP and TAS. In the as-cast film, donor and acceptor phases were well intermixed leading to an ultrafast decay of exciton signal. From the energetic view, this ultrafast fast decay might result from the large driving force (LUMO difference: 0.79 eV) at the heterojunction for charge generation, and agrees with observations in fullerene-based systems. With morphology optimization by solvent type and post annealing treatment in ANQ-based molecules, the domain purity probably increases and phase

segregation improves,^{50,51} supported by previous morphological observations.⁴³ The exciton population obeys a power-law decay, suggesting dispersive exciton diffusion and/or a time-dependent diffusion coefficient⁵². The exact charge transfer rate is not clear, but the charge generation is probably limited by exciton diffusion. This slower exciton dissociation also correlates with slower CTS formation at ~2 ps in annealed film. The efficiency of direct charge generation almost doubled in more ordered film phases, similar to fullerene aggregation case.²⁸ A rather big difference in charge separation efficiency suggests substantial improvement of interfaces for charge separation. In all materials CTSs decay at a similar rate (~130 ps) as observed in PPP and TAS experiments. This indicates that this time scale is inherent independent of the morphology, which is also seen at polymer-polymer interface.⁵³ The invariance of decay to the material composition and processing suggests that states are strongly bound and 'cold' charge generation pathway cannot compete with GR even after morphology optimization. The dominance of fast GR over slow hopping-mediated charge separation mainly limits its charge generation efficiency, agreeing with its low efficiency. This fast GR time scale might come from strong non-radiative recombination of CTSs. The same recombination rate of CTSs regardless of its morphology obtained here may not be applicable to other material blends. We note that the recombination rate of CTSs may also vary with its electron-hole separating distance. However, for excited CTS, either strongly coupled to charge-separated states, or quickly relaxing to its localized CTSs, its lifetime is not easy to measure. The extreme case is the realization of long-lived luminescence from the charge-separated states in exciplexes.⁵⁴

Conclusions

In this work, two ultrafast techniques, pump-push photocurrent spectroscopy and near-infrared transient absorption spectroscopy, were used to elucidate the charge dynamics in photovoltaic devices based on two novel non-fullerene small-molecule acceptors. By changing the solvent type

and the thermal treatment, we observed a large variation in charge separation efficiency. The strong correlation between geminate recombination and device efficiency suggests that geminate recombination is the main limiting process for efficient device operation. This correlation demonstrates the useful nature of the photocurrent-detection technique for guiding device optimization. In-depth investigation by TAS allowed us to identify specific spectral signatures for CTSs and charges and confirmed the observed CTSs generation and recombination rates. This agreement suggests charge separation is not favorable for localized CTSs. The geminate recombination rate is coherent and independent of the morphology. Further optimization of the studied materials should probably focus on facilitating long-range charge separation and avoid the formation of localized charge transfer states. Our investigation of charge dynamics offers new insight into geminate recombination in a family of non-fullerene acceptor materials, and should be of great relevance to the broad community.

Supporting Information Description

Description of Device Fabrication.

Figure S1. Normalized pump-probe spectra of P3HT:DPP-ANQ-DPP films with different processing conditions. (a) Anneal with DCB. (b) As cast with CF

Table S1. Solar Cell Performance of DPP-FN-DPP and DPP-ANQ-DPP based Blends in DCB.

Table S2. Solar Cell Performance of DPP-FN-DPP and DPP-ANQ-DPP based Blends in CF.

Table S3. Summary of Pump-Push Responses of the Studied Material Blends with Different Processing Conditions

Table S4. Sensitivity Comparison of $\Delta J/J$ in Devices with Different Processing Conditions.

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Table of Contents Graphic

Ketonic non-fullerene acceptor

	CHARGE GENERATION	CHARGE SEPARATION EFFICIENCY
Dichlorobenzene Annealing	~130 ps Slow ~2 ps	Relatively high
Chloroform As-cast	~130 ps Ultrafast <200 fs	Extremely low

Charge generation and charge separation efficiency of non-fullerene organic solar cells based on the ketonic non-fullerene acceptor.