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Measurement of the Charge Carrier Mobility Distribution in Bulk Heterojunction Solar Cells

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Organic solar cells have been the focus of extensive research over the past two decades, largely due to their potential to offer an attractive, economically viable pathway to renewable energy production.^[1–3] Most commonly, these “plastic” devices are fabricated in the bulk heterojunction (BHJ) architecture, where the solution-processable photoactive layer comprises two fully percolated, nanoscale, interpenetrating networks consisting of a conjugated polymer or small molecule donor and a fullerene derivative electron acceptor.^[4,5] This blended structure enables efficient, ultrafast charge transfer, and subsequent transport of mobile carriers to the electrodes of the cell.^[6–11] Indeed, despite the tortuous and inherently convoluted nature of the BHJ, advances in molecular design, morphology engineering, and process control^[12–18] have resulted in increasingly high-performance systems with internal quantum efficiencies (IQE) approaching unity under optimal conditions.^[19,20]

In order to improve power conversion efficiency (PCE) then, it is necessary to enhance the quantity of light such solar cells can harvest. One technique involves incorporating low bandgap materials into the photoactive layer, which pushes the absorption edge toward the infrared, resulting in a better overlap of the device's absorption profile with the solar spectrum.^[21–24] A second possibility is to make thicker BHJ active layers. Most optimized BHJ solar cells are optically thin, despite the relatively large absorption coefficients of the materials involved, with thicknesses corresponding to the first constructive interference maximum in the photoactive layer. This leads to significant losses as light passes right through the device. Simply casting a thicker film, however, is often counterproductive, as increased recombination losses during transport result in severely degraded carrier collection efficiency.^[25–27] To combat this, it becomes essential to reduce either recombination rates or carrier transit times. Consequently, the fabrication of thicker solar cells while maintaining a high IQE remains a top priority, as it could immediately lead to marked improvements in device performance.

In order to understand why the device thickness plays such a prominent role in the competition between recombination and sweep-out due to the internal electric field, we first note that for photogenerated charges, the drift velocity is given by $v_{\text{drift}} = \frac{\mu V_{\text{int}}}{d}$, where μ is the carrier mobility, V_{int} is the internal voltage across the cell, and d is the thickness of the light harvesting layer(s). Since each absorbed photon generates an electron and a hole, which drift in opposite directions, each carrier must travel an average distance of $\frac{d}{2}$ for extraction, leading to a characteristic sweep-out time of $\frac{d^2}{2\mu V_{\text{int}}}$. It is evident then, due to the d^2 dependence, that in order to appreciably increase device thickness without also significantly increasing the transit time where carriers are susceptible to recombination, a substantial, simultaneous increase in vertical carrier mobility is required. Note that “vertical” refers to charge carrier transport orthogonal to the plane of the substrate, through the photoactive layer, toward the contacts.

Unfortunately, there is a current lack of truly reliable methods for measuring vertical carrier mobility for BHJ solar cells, which becomes problematic when the need to increase this mobility takes on a central role for device improvement. Field-effect transistor (FET) configurations, time of flight, space charge limited current, and various forms of photo-CELIV (charge extraction by linearly increasing voltage) all enjoy some degree of popularity,^[12,28–34] but none of these techniques by themselves provides an ideal solution. FET measurements are ubiquitous from a materials characterization perspective, but probe lateral instead of vertical transport; the two can differ by

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Figure 1. Solar cell donor materials and steady-state performance. a) Molecular structures and b) the associated J - V characteristics of the materials investigated in this study.

orders of magnitude.^[35] The other aforementioned techniques all require some combination of blocking contacts to prevent injection current, or fabricating extraordinarily thick photoactive layers, ranging up to and over several micrometers, in an effort to enforce surface generation conditions instead of bulk generation under illumination.^[25,28,33] The researcher must then assume that the morphology and transport characteristics of such a thick layer are the same as for an optimized thin

film. Most important, however, is that each of these techniques yields a single number for the carrier mobility. Due to the disordered structure and complex film morphology, transport in BHJ solar cells is highly dispersive. Thus, the details of the distribution of carrier mobilities will have a profound impact on the device performance.

In this paper, we show that with a novel combination of transient photocurrent (TPC) and short circuit variable time-delayed collection field (SCVTDCF) measurements, we can determine the complete vertical mobility distribution for the photogenerated carriers in fully functional BHJ solar cells, allowing for a much richer visualization of the transport dynamics than was previously possible. We demonstrate the versatility of these techniques on four optimized devices, applying them to polymer and small molecule donors, as well as conventional and inverted configurations. **Figure 1a** shows the materials which were blended with [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₁BM) for the solar cells in this investigation. The associated steady state current-density voltage (J - V) curves are displayed in **Figure 1b**, and the relevant device figures of merit are summarized in **Table 1**.

Solar cells were fabricated according to the procedures outlined in the Experimental Section. PTB7-Th (Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-*co*-3-fluorothiopheno[3,4-*b*]thiophene-2-carboxylate]), a high-performance polymer,^[36] was chosen as the material to highlight the conventional and inverted geometries. As seen in **Table 1**, the overall performances of the two PTB7-Th cells were largely similar. These were compared to *p*-DTS(FBTTh₂)₂ (7,7'-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole)), which is widely known as a small molecule donor that has proven itself to be a competitive alternative to many polymer-based solar cells.^[17] Finally, the study was rounded out with PPDT2FBT (poly[(2,5-bis(2-hexyldecyloxy)-1,4-phenylene)-alt-(5,6-difluoro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole)]), which was recently shown to stand out as an exceptional polymer system capable of retaining superior PCE despite being constructed with unusually thick BHJ active layers.^[37] The PCE of our optimized PPDT2FBT solar cell was 8.1% with a noteworthy 350 nm photoactive layer, which was more than three times thicker than that of the other devices.

These four solar cells were first investigated through TPC measurements, which represent a powerful means of probing charge carrier transport and recombination kinetics. As a time-resolved technique, TPC is capable of yielding detailed insights into the charge carrier density, mobility, the density of states, and recombination mechanisms in ways that are

Table 1. Relevant solar cell figures of merit for all devices in this study from steady state J - V and TPC measurements. Note that the thickness column represents the total thicknesses of the solar cells between their electrodes, including any transport/blocking layers as well as the photoactive layer.

Solar cell donor material	J_{sc} [mA cm ⁻²]	V_{oc} [V]	Fill factor [%]	PCE [%]	V_{BI} [V]	Thickness [nm]	μ_{max} [cm ² V ⁻¹ s ⁻¹]
PTB7-Th	18.2	0.77	62	8.8	0.94	120	0.0016
PTB7-Th Inverted	15.6	0.78	67	8.1	0.87	140	0.0026
<i>p</i> -DTS(FBTTh ₂) ₂	13.5	0.76	70	7.2	0.88	140	0.0030
PPDT2FBT	16.6	0.76	64	8.1	0.81	380	0.018

largely inaccessible via most steady-state approaches.^[14,34,38–45] In order to perform such experiments, charges are first photogenerated in the solar cell by a brief pulse of light with temporal width much shorter than the carrier transit time through the BHJ material. Following excitation and charge transfer, the mobile carriers are then driven toward their respective electrodes by the internal electric field, which can be varied through the application of an external DC voltage bias (V_{bias}). The total internal potential (V_{int}) across the device determines the drift velocity of the carriers and the temporal profile of the photocurrent extraction. It is given by

$$V_{\text{int}} = V_{\text{BI}} - V_{\text{bias}} \quad (1)$$

where V_{BI} is the built-in voltage of the cell. For each device, V_{BI} was established by finding the external bias point where the photocurrent changes sign.

The transport of photogenerated carriers through such an inhomogeneous medium must be described by multiple trapping in a distribution of localized states.^[39,46] As such, there exists some population of carriers with a well-defined maximum mobility, μ_{max} , while the rest exhibit a distribution of mobilities due to repeated trapping and release. Unless a trapped charge recombines, the energetic depth of a trap is statistically correlated with the time the carrier is immobilized before being thermally released.^[39,40,43] In such disordered materials, the resulting spread of average carrier velocities and transit times results in dispersive transport with a physical and measurable manifestation being a time-dependent mobility.

A simplified schematic of the experimental setup used to perform the TPC/SCVTDCF measurements is shown in **Figure 2**, with a detailed description of the apparatus found in the Experimental Section and in a previous publication.^[38] A nitrogen pumped dye laser was used as the excitation source, which provided 4 ns wide, $\lambda \approx 590$ nm pulses with a repetition rate of 10 Hz. A set of computer-controlled, variable neutral density filters determined the intensity of the incident light, of which half was sent to a photodiode energy meter that monitored every pulse. This enabled a typical measurement to consist of 500 current transients averaged together, where no pulse deviated by more than 3% from the target fluence of $0.06 \mu\text{J cm}^{-2}$. An

automatic shutter, which was essential for the dark SCVTDCF measurements, was used to physically block the light from the solar cells when necessary. The time-resolved photocurrent was recorded on a 300 MHz oscilloscope by measuring the voltage drop across a small, 5Ω RF sensor resistor in series with the device. Finally, the bias source for the TPC measurements was an Agilent 33519B waveform generator operating in DC mode, connected to the cell through a wideband bias tee. For the SCVTDCF measurements, the bias source was switched to a digital delay generator, whose output stage has been modified for low impedance output. The overall RC time constant of the entire circuit was measured to be less than 5 ns, allowing for excellent resolution of the transient kinetics on timescales that are usually completely inaccessible via TPC techniques.

Transient photocurrent measurements were performed on the aforementioned solar cells at room temperature, with the bias-dependent results displayed in **Figure 3**. Parts (a)–(d) of **Figure 3** show the TPC traces for each of the devices, with the insets revealing the long photocurrent tails that are an unmistakable signature of dispersive transport. Note that a negative voltage corresponds to a reverse bias, which increases the internal field of the solar cell. Assuming that the mobility is not a function of position within the BHJ (no donor/acceptor concentration gradients), that space charge effects are negligible due to the low-level excitation, and that the illumination uniformly gives rise to a homogeneous distribution of carriers across the active layer, then the current density at time t for each carrier type, $J_i(t)$, is expressed as^[38,44]

$$J_i(t) = \left(\frac{qn_i(t)\mu_i(t)V_{\text{int}}}{d} \right) \left(1 - \frac{\mu_i(t)V_{\text{int}}t}{d^2} \right) \quad (2)$$

where $i = n, p$, and $n_i(t)$ is the internal carrier density of the specified type. The total photocurrent through the cell is the sum of the electron and hole currents.

We begin by following the analysis procedure outlined in a prior manuscript.^[38] At very short time scales after photoexcitation, prior to any significant recombination, $n_i(t) = n_i(0) = \frac{1}{2}n_0$, where the factor of $\frac{1}{2}$ arises because electrons and holes each individually make up half of the initial carrier density, n_0 . We can estimate n_0 by integrating the photocurrent transient for each solar cell under high reverse bias. Since the time integral of the photocurrent yields the total number of extracted carriers, and recombination in an efficient solar cell is minimal under the influence of a large internal field, this provides an accurate estimate of the initial carrier density.

Additionally, we assume that the first carriers to be extracted are those with the largest drift velocity, and hence those with mobility μ_{max} , since the effects of dispersive transport have not yet had time to manifest. Therefore, by setting $\mu_i(t) = \mu_i(0) = \mu_{\text{max}}$, and $n_i(t) = \frac{1}{2}n_0$, Equation (2) predicts the current density to fall off linearly at short time scales. This is clearly seen in **Figure 3a–d**, and explicitly demonstrated in **Figure S1** in the Supporting Information. For all measured values of the internal field, the initial photocurrent decay has a linear regime in each device. This is consistent with bulk generation of mobile carriers all moving with an initial constant drift velocity, determined by μ_{max} and the internal fields of the respective devices. In addition, resolution of the linear decay is

Figure 2. Diagram of the TPC/SCVTDCF system. Simplified schematic of the experimental setup used for transient photocurrent and short circuit variable time delayed collection field measurements.

Figure 3. TPC and internal conductance measurements for each solar cell. Bias-dependent transient photocurrent measurements on the a) conventional architecture PTB7-Th, b) inverted configuration PTB7-Th, c) p -DTS(FBTTh₂)₂, and d) PPDT2FBT solar cells. The insets display the photocurrent tails which are indicative of dispersive transport. Internal conductance plots for each material show the TPC traces normalized by their own internal potentials, presented respectively in (e–h).

unambiguous proof that the measurements are not RC limited, as otherwise one would observe the photocurrent dropping off exponentially with an RC time constant equal to that of the measurement apparatus.

By fitting the slopes of the linear regimes of the TPC traces under these short timescale approximations, we can determine an upper bound for the vertical carrier mobility for each device, the results of which are shown in Table 1. It is immediately apparent from this calculation that $\mu_{\max}$ of the PPDT2FBT material is roughly an order of magnitude higher than that of the other systems, which is consistent with the earlier observation of high performance despite an unusually thick photoactive layer.

It is important to note that there is no evidence whatsoever of well-defined or separate timescales for collection of the two different carrier species in any of the TPC traces, regardless of whether the solar cell is based on polymers or small molecules, or is fabricated in the conventional or inverted configuration. We are therefore unable to measure distinct electron and hole mobilities with this technique. However, asymmetric carrier extraction is incompatible with efficient solar cells, as transport would be largely inhibited by the rapid generation of an internal space charge. As such, we expect the individual carrier mobilities to be balanced and self-consistently comparable, and therefore the resulting determination of $\mu_{\max}$ is descriptive of both electrons and holes.

Given the equality of the electron and hole mobilities, we can rewrite Equation (2) as

$$J_T(t) = \left(\frac{qn(t)\mu(t)V_{\text{int}}}{d} \right) \left(1 - \frac{\mu(t)V_{\text{int}}t}{d^2} \right) \quad (3)$$

where $J_T(t)$ is the total photocurrent and $n(t)$ is the total internal carrier density. Continuing with the short timescale approximations, we set $t = 0$ to be the peak of the photocurrent traces. Equation (3) then becomes

$$J_T(0) = \frac{qn(0)\mu(0)V_{\text{int}}}{d}$$

$$\frac{J_T(0)}{V_{\text{int}}} = \frac{qn_o\mu_{\max}}{d} \quad (4)$$

Therefore, by normalizing each of the bias-dependent TPC curves for each of the devices by their own respective internal potentials, it is evident from Equation (4) that if both the initial carrier density and the maximum carrier mobility are independent of the internal field, then the peaks of the photoconduance traces should all collapse to the same point, as $\frac{qn_o\mu_{\max}}{d}$ would be a constant quantity with respect to the field. Figure 3e–h shows this to be true for all four of the solar cells

with remarkable accuracy. The only device with any real deviation is the p -DTS(FBTTh₂)₂ based cell, which can be attributed to an imperfect measurement of V_{BI} , and even still, the variation is slight.

The primary implication of this observation is that it shows geminate recombination via bound charge transfer excitons to be almost completely absent in all of these solar cells, since the initial carrier density is independent of internal field over an order of magnitude of field strength. If this were present as an efficient photocurrent loss mechanism, then as the internal field increased, polaron pair dissociation would also increase, resulting in a field-dependent initial carrier density. We suggest then that the charge transfer state must therefore either have a binding energy comparable to or less than thermal energy, in order to undergo efficient separation at all internal fields, or must not be bound at all. The coulombic attraction between the electrons and holes could instead yield a resonance state comprised of mobile carriers in their respective domains.^[6,10] In a prior publication,^[38] we came to a similar conclusion for a different small molecule based BHJ solar cell, so we have now demonstrated this phenomenon in two different small molecule systems, two different polymer systems, and in both conventional and inverted configurations. This strongly indicates that our findings possess general applicability for high-performance solar cells.

We have extracted significant value from the transient photocurrent measurements, but the utility of the technique would be greatly enhanced if we could model Equation (3) directly without restricting our analysis to short timescales. Unfortunately, without making more assumptions, we are inherently limited with TPC measurements alone, as we encounter the problem of incomplete information. Since BHJ solar cells are optically thin, carriers are generated throughout the bulk of the photoactive layer. The simultaneous presence of both charge species allows for non-geminate recombination, which has the potential to take many forms. This can include bimolecular recombination, usually described as Langevin recombination with a significantly reduced rate constant compared to that predicted by the original Langevin theory, or it can be trap-assisted, Shockley–Read–Hall recombination.^[45,47,48] There have even been reports of higher order processes.^[32,49] This causes the internal carrier density, $n(t)$, to decay with a functional form and magnitude that is not known a priori, and which cannot be determined by TPC measurements alone. In addition, we have shown carrier transport to be highly dispersive, with the distribution of carrier mobilities dependent on the density of states. We therefore have one equation with two unknowns, but if we could independently determine either the internal carrier density or the mobility as a function of time, then we could solve for the other, as it can be trivially calculated from Equation (3).

Here, we show that by combining our previous transient photocurrent results with short circuit variable time-delayed collection field measurements, we are able to experimentally obtain an independent, numerical determination of the time dependence of the internal carrier density, $n(t)$, for each device. This allows for calculation of $\mu(t)$, and from that, a subsequent comprehensive determination of the mobility distribution for the photogenerated carriers in the four fully functional, optimized solar cells. Such information presents a much more

complete picture of the transport dynamics of the cells than a single mobility value ever could, as these distributions heavily influence many of the fundamental processes that occur within the solar cells.

SCVTDCF measurements are very similar to the TPC experiments we have previously described, with the critical caveat that the internal field of the solar cell is not held constant throughout the course of the measurement. Instead, the DC bias source (V_{bias} in Figure 2) is replaced with a digital delay generator (DDG) that can output either 0 or 5 V, and more importantly, can switch between the two very quickly, and with extraordinarily precise timing. This means that as before, we can hold a solar cell at short circuit condition, use the laser pulse to photoexcite carriers, and then measure the time resolved extraction, essentially identically reproducing our prior short circuit TPC measurements. The difference is that after the photogeneration, at any variable delay time t , we can quickly switch the delay generator to a high reverse bias condition and sweep out all of the remaining carriers inside the device under the influence of the collection field.

Since recombination is minimal under high internal field conditions in efficient devices, the number of carriers extracted from the solar cell after the clearing pulse is applied is an accurate estimate of the number of carriers that were present inside the device when the voltage was switched. Consequently, this is a direct measurement of the internal carrier density at that time t . By then repeating this experiment many times with differing variable time delays, we can numerically determine $n(t)$ with all the effects of recombination and carrier extraction already built in, without knowing the relevant processes themselves a priori.

The DDG itself is capable of switching the bias on the solar cell in less than 1 ns, and can do so for any variable time between negative delay (before the laser pulse hits the cell) out to 10 s after the photoexcitation, with resolution of better than 50 ps. We therefore have total control over when the collection field is applied, and there is no part of the transient photocurrent trace that is inaccessible to this experiment.

Figure 4a provides an illustration of how to measure the photocurrent with the SCVTDCF technique. As can be seen, a large background capacitive pulse results from stepping the bias voltage from 0 to 5 V. However, by using the shutter shown in Figure 2 to block the laser from the solar cell, we can alternately perform this measurement in the light and the dark and then subtract out the capacitive pulse, yielding only the photocurrent. An example of the result of this procedure is shown in Figure 4b for a single delay time, t . It is evident from the second peak in the photocurrent trace (red) that when the time-delayed collection field pulse (black) is applied to the solar cell, the carrier extraction is enhanced, and it is from this point on that the time integral is computed to determine $n(t)$ (blue). Since we showed with our prior TPC measurements that the carrier generation in each of these devices is independent of the internal field, we are confident that the increased photo-carrier extraction is due to suppressed recombination from rapid sweep-out under the influence of the high internal field. Our earlier measurements prove that we are not generating additional carriers with this technique, but merely efficiently sweeping out the mobile carriers that already exist, validating our measurement of $n(t)$.

Figure 4. Using SCVTDCF measurements to determine $n(t)$. a) Isolating the SCVTDCF photocurrent from the capacitive current by subtracting off a dark measurement from a light measurement to show b) a typical SCVTDCF trace. Repeating this measurement at many temporal points along the short circuit TPC curves for each solar cell yields the internal carrier density as a function of time, $n(t)$, for each of the devices, at c) short and d) long timescales.

For each of the devices in this study, the SCVTDCF measurement of $n(t)$ was repeated from negative delay times out to 600 ns in steps of 2 ns (Figure 4c), and again in steps of 10 ns out to 3000 ns (Figure 4d), where we approach the noise floor of our instrumentation. Combining these measurements together generates a high-resolution numerical determination of the time-dependent internal carrier densities with no assumptions being made about recombination mechanisms, and no restrictive, short timescale approximations. It is important to note that the PPDT2FBT cell exhibits a lower initial carrier density when compared to the other devices, because the thickness is approximately three times that of the other solar cells. The laser fluence was the same for all four of the devices, but the photogenerated carriers in the PPDT2FBT device were distributed over a larger volume, resulting in the lower initial carrier density.

At this point, for all four of the solar cells, we have $J_T(t)$ from TPC, $n(t)$ from SCVTDCF, and both the device thickness and V_{int} are known. By combining the complementary techniques of TPC and SCVTDCF, Equation (3) is then easily numerically solved for $\mu(t)$ at each point in time for each device. The resulting time dependence of the mobility, shown in Figure S2 (Supporting Information), is the physical manifestation of the distribution of carrier mobilities in the solar cells. Determining these distributions is our primary goal, as they strongly influence the device performance.

We use the time-dependent mobilities that were just calculated to determine the full mobility distributions by going back to the short circuit photocurrent traces for each of the four solar cells and by determining how many carriers were extracted for each mobility value. Since the integral of the photocurrent trace over any window of time yields the number of carriers that were extracted during that window, we divide the photocurrent traces into discrete intervals of time around each SCVTDCF data point limited only by the resolution of the SCVTDCF measurements,

which in this case is every 2 ns. It is then entirely reasonable to approximate that the carriers extracted in the 2 ns window around any time t all had the same mobility as was determined by Equation (3) for that same time t , and by repeating this process over the entire TPC trace, we can build a histogram of the carrier mobilities within the cells.

Figure 5 shows the resulting vertical mobility distributions of each of the four solar cells, and compares them to the upper bound values of μ_{max} previously calculated from TPC alone (dashed lines). We see once again that the vertical carrier

Figure 5. Mobility distributions for all four solar cells. Histogram of the mobilities of the photogenerated carriers with comparisons to the μ_{max} values calculated from TPC measurements alone (dashed lines).

mobility of the PPDT2FBT device is significantly higher than that of the other cells, confirming our original observations, and once again suggesting that this mobility is the reason that PPDT2FBT is capable of maintaining high PCE despite an unusually thick photoactive layer. We also see that even though we made several assumptions in the short timescale approximations of μ_{max} that served to maximize the calculated values, the final results were close to the peak mobilities as determined by the combination of TPC and SCVTDCF, which did not suffer the same limitations.

It is immediately evident from these mobility distributions how limiting a single number for carrier mobility can be when viewed in the context of understanding the transport characteristics in a highly dispersive material. Indeed, it is clear from these results that transport is not well described by a single, effective mobility value. This work presents an alternative to such approximations, which can be very useful for theoretical modeling. The width and overall shape of the distributions in Figure 5 can be used to gain insight into the density of states and will be one of the primary factors that govern transport and recombination. Such detailed modeling is beyond the scope of this manuscript, but will be addressed in future work.

In this contribution, we have outlined a procedure to combine transient photocurrent and short circuit variable time-delayed collection field measurements in such a way so as to calculate the complete vertical mobility distributions for the photogenerated carriers in functional, fully optimized solar cells. This allows for a much richer visualization of the transport dynamics than was previously possible through other measurement techniques, and was accomplished without the need for blocking contacts or enforcing surface generation conditions. We have demonstrated these techniques on polymer and small molecule solar cells, as well as in the conventional and inverted configurations, thereby ensuring the broad applicability for determining the critical parameters required for understanding charge transport through BHJ solar cells. In addition, we showed that field-dependent carrier generation is nonexistent in all of these systems. This implies the general conclusion for high performance BHJ solar cells that geminate recombination via charge transfer excitons is absent as a loss mechanism, and suggests that the charge transfer state intermediary in the carrier generation process does not have a binding energy significantly greater than thermal energy.

Experimental Section

Device Fabrication and Steady-State Characterization: PTB7-Th and *p*-DTS(FBTTh₂)₂ were purchased from 1-Material Inc. PC₇₁BM was purchased from Solenne BV. The synthesis of PPDT2FBT was reported previously.^[37] All materials were used as they arrived. Solar cells were fabricated on cleaned ITO-coated glass substrates. The substrates were first scrubbed with detergent, and then sequentially ultrasonicated in water, acetone, and isopropyl alcohol, before drying overnight in an oven. Directly prior to fabrication, the substrates were UV-ozone treated for 15 min. For the inverted PTB7-Th cell, a sol-gel-derived ZnO precursor solution^[18] was spin-cast at 4000 rpm for 40 s onto the substrate and then heated to 220 °C for 40 min in air. PTB7-Th:PC₇₁BM (1:1.5 w/w, 3% DIO v/v) in chlorobenzene (total concentration of 25 mg mL⁻¹) was deposited on the ZnO by spin-coating at 1300 rpm for 40 s, and was subsequently heated at 70 °C for 10 min in order to drive off any

residual solvent. MoO₃ (≈5 nm) and Ag (≈100 nm) were deposited via thermal evaporation to complete the anode. For the conventional structure devices, PEDOT:PSS (Baytron PH for the *p*-DTS(FBTTh₂)₂, Clevis P VP Al 4083 for the PTB7-Th and the PPDT2FBT) was first spin cast at 5000 rpm onto the treated ITO substrates for 40 s (30 s for the PTB7-Th cell). The PEDOT was dried at 140 °C (150 °C for PTB7-Th cell) for 10 min in air. The photoactive layers for the three cells were deposited as follows: PTB7-Th:PC₇₁BM was spin-cast at 1000 rpm for 60 s using the previously described solution preparation conditions. No post-deposition annealing was performed. *p*-DTS(FBTTh₂)₂:PC₇₁BM (1.5:1 w/w, 0.4% DIO v/v) in chlorobenzene (total concentration of 35 mg mL⁻¹) was spin-cast at 1700 rpm for 40 s, and subsequently heated to 70 °C for 10 min. PPDT2FBT:PC₇₁BM (1:1.5 w/w, 2% diphenyl ether v/v) in chlorobenzene (total concentration of 70 mg mL⁻¹) was spin-cast at 3000 rpm for 40 s, and subsequently placed in vacuum to drive off residual solvents. For the *p*-DTS(FBTTh₂)₂ cathode, 10 nm Ca was deposited via thermal evaporation, followed by 100 nm of Al. For the other devices, only the Al was used. All contacts were deposited under high vacuum between 3 × 10⁻⁶ and 6 × 10⁻⁶ Torr. For each of the solar cells, the 3.25 mm² geometrical overlap of the top contact with the ITO defined the active area. See Figure S3 (Supporting Information) for the solar cell electrode geometry. A Keithley 2400 SourceMeter was used to measure steady state *J*-*V* curves for each of the four solar cells, under illumination from a Newport AM 1.5G full spectrum solar simulator calibrated to an intensity of 100 mW cm⁻². Masks (1.70 mm²) made of thin black plastic were attached to each cell prior to measurement of the *J*-*V* characteristics in order to accurately measure the device performance. All cells were tested in air after UV-epoxy encapsulation.

Transient Photocurrent Measurements: TPC measurements were taken with a custom-built, fully automated setup. A Stanford Research Systems NL100 nitrogen laser provided the excitation source for photocurrent generation by pumping a cuvette of Rhodamine 6G laser dye housed within an attached dye cell. The pulsed dye laser produced 4 ns wide, $\lambda \approx 590$ nm pulses with a repetition rate of 10 Hz. A 50/50 beam splitter simultaneously sent every pulse to a Coherent J-10Si-le energy sensor as well as the solar cell under test, which allowed a computer-controlled variable neutral density filter wheel to set and actively monitor the incident light intensity. The active monitoring of the fluence of every pulse allowed a typical measurement to consist of 500 current transients averaged together, where no pulse deviated by more than 3% from the target fluence of 0.06 $\mu\text{J cm}^{-2}$. The external voltage bias was applied to the solar cell with an Agilent 33519B waveform generator operating in DC mode, connected to the cell through a wideband bias tee. Since it was imperative in TPC measurements to aggressively minimize circuit series resistance wherever possible, the bias tee was an essential, but easily overlooked component, as it provided a high-frequency shunt for the TPC pulse. This dramatically reduced the RC time constant of the circuit, and prevented the bias source itself from interfering with the measurement. In addition, the RC time constant was further diminished by careful design of the solar cell geometry, with the small area decreasing capacitance, and close proximity of the anode and cathode curtailing the series resistance. From Figure 3a–d, it is evident that the rise time of the solar cell is a good indication of our temporal limitations, since it is the fastest, highest frequency feature of the TPC traces. This rise time was limited by the RC constant of the system as a whole, including the solar cell itself, as well as the external measurement circuit, and from this rise time, our RC constant is determined to be better than 5 ns. The time-resolved photocurrent was recorded on a 300 MHz Tektronix DPO3034 oscilloscope by measuring the voltage drop across a surface mounted, 5 Ω RF sensor resistor (so as to not attenuate high-frequency signals) in series with the device. 5 Ω was selected to further minimize the RC time constant of the setup.

Short Circuit Variable Time Delayed Collection Field Measurements: With the exception of the external voltage bias source, SCVTDCF measurements were carried out in an identical manner to the TPC measurements previously described. For the SCVTDCF measurements, however, both the waveform generator and the wideband bias tee were removed and replaced with a Highland Technology T560 digital delay

generator whose output stage was modified for low source impedance. In the absence of the bias tee, which would oppose the rapid voltage changes that were integral to the SCVTDCF measurement, the modified output stage of the T560 was necessary to maintain low RC time constants.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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