Polarization Dependence of Charge Conduction in Conjugated Polymer Films Investigated with Time-Resolved Terahertz Spectroscopy

Timothy J. Magnanelli,1 Sebastian Engmann,1,3 Jared K. Wahlstrand,1 John C. Stephenson,1 Lee J. Richter,2 and Edwin J. Heilweil1,*

Physical1 and Material2 Measurement Laboratories, National Institute of Standards and Technology (NIST), Gaithersburg, MD, 20899, USA

3Theiss Research, La Jolla, CA, 92036, USA

ABSTRACT

Room temperature Time-Domain Terahertz (TDS) and Time-Resolved Terahertz (TRTS) spectroscopic methods are employed to measure carrier mobility and charge generation efficiency in thin-film semiconductor polymers. Interrogation of the dependence on excitation and probe polarizations yields insight into the underlying material properties that guide charge transport. We apply THz polarization anisotropy probes to analyze charge conduction in preparations of the copolymer PCDTPT, consisting of alternating cyclopenta-dithiophene (donor) and thiadiazolo-pyridine (acceptor) units. Comparisons are made among films of different ordering and morphology, including aligned films prepared by blade
coating, a near isotropic dropcast film, and isotropic liquid dispersion. They are further contrasted with their population dynamics ascertained through transient absorption and the traditional photoconductive polymer poly-3-hexylthiophene (P3HT). Polarization anisotropy is observed as preferential charge conduction along the backbone propagation direction of PCDTPT, with various factors disproportionately influencing directional mobility and charge pair yield. PCDTPT exhibits unexpectedly strong conductivity when isolated in toluene dispersion. Quantitative comparisons yield a better understanding of polaron/free-charge relaxation and transfer mechanisms and illustrate dynamics among photoexcited charge carriers and their motion and diffusion through different material morphologies.

INTRODUCTION

Conjugated polymers are versatile materials with a plethora of applications in organic versions of field effect transistors, photovoltaic devices, and related opto-electrical components. Improvement in their functionality, efficiency, and operability hinges on clarifying how polymeric charge conduction pathways are affected by morphology (local ordering) and anisotropic polymer organization relative to their environment. The introduction of short-contact polymers\(^1\) has provided a new avenue of study for polymer transistors, with multiple systems achieving high mobilities in excess of 5 cm\(^2\)V\(^-1\)s\(^-1\).\(^2\) Evidence increasingly points to prevalent heterogeneity in high-performing semiconductor polymer films, with rapid transport in well-ordered regions limited by tie-chains\(^3\text{-}^5\) or inter-chain contacts.\(^6\) The intrinsic anisotropy of charge transport along the conjugated polymer backbone in well-ordered regions has led to considerable interest in the exploration and manufacture of aligned films to enhance device performance.\(^7\text{-}^8\) Non-contact probes of conductivity, including Time-Resolved Microwave Conductivity (TRMC)\(^9\text{-}^{11}\) and Time-Resolved Terahertz (THz) Spectroscopy (TRTS),\(^12\text{-}^{13}\) are powerful tools for interrogating the intrinsic properties of well-ordered regions in semiconductor polymer films. Both
TRMC and TRTS primarily report on the aggregate mobility of electron and hole charge carriers populated in a sample following polarized photoexcitation and separating electron and hole responses requires additional experimentation and intricate modeling. TRMC has been shown to report on conduction activity over shorter length scales (with higher mobilities) than contact based measurements;\textsuperscript{14} this effect occurs more prominently for TRTS,\textsuperscript{15} providing more in-depth and localized insight into short-contact polymers. In this report, we apply polarization resolved TRTS and transient absorption (TA) to the study of PCDTPT, a high-performing short-contact copolymer that can be aligned through blade coating approaches.\textsuperscript{16}

\textit{Polarization Anisotropy}

Polarized photoexcitation sources instill time-dependent, geometric anisotropies into the dipoles of transient state populations, which revert towards isotropy prior to relaxation to their ground state. This anisotropic decay reflects a combination of the rotation of a molecule within solution or gas phase,\textsuperscript{17–19} systematic offset of a dipole following charge/energy transfer events,\textsuperscript{20,21} and changing nature of the overlap between dipoles with excited states of the potential energy landscape as seen in polarized fluorescence, transient absorption, and related experiments.\textsuperscript{18,19,22–24} These effects indicate how polarization anisotropy can depict the dynamics of electronic transients and their reliance on the local molecular structure and environment.\textsuperscript{22,25} Previous studies highlighted morphological effects on polarized charge conduction\textsuperscript{26,27} and explored the directional dependencies and dynamics of electronic transient state populations using polarized spectroscopies.\textsuperscript{28} Anisotropic phenomena have also been observed in systems interrogated using THz pulses.\textsuperscript{29} A routine metric for measuring the time-dependent polarization anisotropy, \( r(t) \), is generalized by Equations 1a and 1b for systems involving three- and two-dimensional degrees of freedom, respectively:
Here, $S$ is the polarization dependent signal recorded parallel ($\parallel$) or perpendicular ($\perp$) relative to a static heterogeneity or field involved in an experiment (i.e., excitation or probe polarization). These signals are typically intensities ($I(t)$) as seen in steady state absorption, photoluminescence, or TA signatures. For an isotropic 3D system, including isolated polymer dispersions and unordered polymer films, the limits of $r_{3D}(t)$ are 0.4 and -0.2 for probed transitions with dipoles completely parallel and perpendicular to the excitation dipole, respectively. Anisotropic limits for an isotropic 2D system, as for layered nanomaterial structures (e.g., aligned or self-organizing polymer films) are +/- 0.5. This difference in 3D and 2D limits arises from two and one orthogonal geometry(ies) being represented by the perpendicular measurement, respectively. However, conduction anisotropy as applied in a TRTS measurement is derived from analysis of the electric field ($E(t)$) of the pulsed THz probe, not the intensity. The linearization of the electric field anisotropy is different from fluorescence or TA anisotropy since the electric field interaction of THz probe pulses with the sample scales as $\cos(\theta)$ rather than $\cos^2(\theta)$ for an angle $\theta$ between the excitation and probe dipoles. This effects both the linearization and anisotropic limits from isotropic media, which become 0.25 and -0.125 and +/- 0.3, for the 3D and 2D cases, respectively. Each limit increases in magnitude for anisotropically ordered/aligned systems, in which the response can approach purely parallel or perpendicular response, leading to theoretical anisotropy limits of 1/-0.5 or +/- 1 for 3D or 2D systems, respectively. These higher limits occur regardless of whether an intensity or electric field probe metric is used.

These determinations provide a direct comparison to anisotropy metrics of charge conduction obtained for a material incorporated into a thin-film transistor. Interrogating polarization anisotropy via THz probe pulse interactions with photoinduced charge carriers entails two considerations.
Foremost, we must decouple anisotropic effects caused by polarized excitation from those based on anisotropic order, morphology, and macromolecular structure built into a given film sample. Additionally, we need to distinguish between different characteristics of charge carrier (polaron) conduction that result in preferential directionality. Accomplishing this requires measuring four different configurations of the photoexcitation (pump) and detection (probe) pulse polarizations relative to an anisotropic sample orientation and a comprehensive model for sample photoconductivity.

**Frequency Dependent Modeling of Photoconductivity**

Time-domain THz (TDS) and TRTS experiments extract the complex THz electric field, $\hat{E}(\omega)$, transmitted through a sample with and without photoexcitation and measured simultaneously. Processing these yield electric field responses of the unexcited sample, $\hat{E}_0(\omega)$, and the difference induced by photoexcitation, $\Delta\hat{E}(\omega)$. The frequency-dependent, complex photoconductivity, $\sigma(\omega)$, is calculated using Equation 2 by directly comparing the photoexcited, $\hat{\eta}(\omega)$, and unexcited/ground state, $\hat{\varepsilon}(\omega)$, dielectric permittivity signals obtained for each polymer sample.$^{34}$

$$\Delta\sigma(\omega) = i \varepsilon_0 \omega (\hat{\eta}(\omega) - \hat{\varepsilon}(\omega))$$  \hspace{1cm} (2)

Here, $\varepsilon_0$ represents the vacuum permittivity and $\omega$ the angular frequency. The implementation of relevant equations to convert from the experimental observables $\hat{E}_0(\omega)$ and $\Delta\hat{E}(\omega)$ to the dielectric functions $\hat{\eta}(\omega)$ and $\hat{\varepsilon}(\omega)$ are included in the SI and described in Equations S1-S3.$^{34}$ Both the real and imaginary parts of the frequency-dependent conductivity are simultaneously fit as a function of frequency using the Drude-Smith model given in Equation 3.$^{15,35}$

$$\sigma(\omega) = \frac{\Delta Nq^2}{m^*} \frac{\tau}{1 - i\omega \tau} (1 + \frac{c_1}{1 - i\omega \tau})$$  \hspace{1cm} (3)
The Drude-Smith model is well-established for succinctly describing semiconducting polymers and confined carriers and drawing conclusions about bulk conductivity.\textsuperscript{15,35} The model represents the frequency-dependent dielectric perturbations by free carriers which rebound off scattering sites within a lattice or randomly oriented medium. The frequency of scattering is represented by a scattering/collision time (τ) between events and can be converted to an average distance traveled if the ballistic velocity of the charges is known. The real and imaginary photoconductivity are simultaneously fit by Equation 3 via nonlinear least squares regression as a function of charge carrier density (ΔN), scattering time (τ), and a backscattering parameter (c\textsubscript{1}). Provided the effective mass (m*) is known, these parameters allow estimation of the total charge mobility (µ) and efficacy of charge separation (Φ\textsubscript{eff}).\textsuperscript{15} Values for Φ\textsubscript{eff} are determined by comparing ΔN to the empirically measured number of photons absorbed, for each sample and pulse polarization configuration. This model cannot directly extract m* values since it cannot be isolated via determination of ΔN and µ (or τ). It also cannot be gleaned from other measurements, so its value must be assumed to proceed with further analysis.\textsuperscript{15}

Direct comparison of τ between morphological directions would avoid uncertainty introduced by non-uniform m*, though predicting µ provides a direct handle on a measurable quantity in devices, does not complicate incorporating c\textsubscript{1} to predict delocalized effects, and is still separate from effects on Φ\textsubscript{eff}. Mobility is determined using Equation 4a\textsuperscript{15,36} at the early delay “peak” and later delay “tail” of the time-dependent traces of the photoexcited conduction signal, yielding µ\textsubscript{P} and an estimate of thermally relaxed limit, µ\textsubscript{T}, respectively. Given the higher uncertainty of the tail signals, we primarily consider signals collected at the photoconductive peaks. Extrapolating the real part of \( \hat{\sigma}(\omega) \) back to 0 THz as the limiting delocalized frequency of Drude-Smith conduction (µ\textsubscript{PDS} and µ\textsubscript{TDS}, Equation 4b) is a more accurate estimate of the combined carrier mobility extrapolated over a macroscopic distance, though each figure conveys slightly different information.\textsuperscript{15} As both µ\textsubscript{P} and µ\textsubscript{PDS} are derived from an inherently localized probe that is sensitive to the most conductive regions of the polymer matrix, they downplay the effects
of grain boundaries and intermittent disordered sub-domains that typically dominate device mobility measurements. This yields the orders of magnitude difference between values reported from TRTS, TRMC, and transistor measurements, the latter of which is also prone limitations in applying contacts.\textsuperscript{15,37}

\begin{equation}
\mu_p, \mu_T = \frac{e\tau}{m^*} \quad (4a)
\end{equation}

\begin{equation}
\mu_{PDS}, \mu_{TDS} = \frac{e\tau}{m^*} * (1 + c_1) \quad (4b)
\end{equation}

**Investigated Polymer Samples**

The conjugated, conductive polymers compared in this study are a copolymer consisting of alternating donors (cyclopenta-dithiophene) and acceptors (thiadiazolo-pyridine, PCDTPT) and the well-studied poly-3-hexylthiophene (P3HT). Their molecular structures are presented in Figure 1a along with their full IUPAC names. PCDTPT exhibits high performance as a short-contact polymer and can be readily aligned onto a substrate, resulting in highly anisotropic and efficient thin-film transistor performance.\textsuperscript{33,38} It also produces a stronger conductive TRTS signals than other polymers considered due to its high mobility and formation of thicker samples. P3HT serves primarily as a basis of comparison to PCDTPT and has been extensively studied by time-resolved conduction analyses.\textsuperscript{15,39} Despite PCDTPT dramatically outperforming P3HT as an organic transistor,\textsuperscript{40} it exhibits poor performance as a spin-coated organic photovoltaic, limited by a low short-circuit carrier density and higher open circuit voltage than a comparable P3HT film.\textsuperscript{41,42} If morphological ordering can improve the transistor performance of PCDTPT by an order of magnitude\textsuperscript{33} and enhancements occur with thermalization\textsuperscript{42} and alignment (slight)\textsuperscript{43} for P3HT, this work explores how ordering can yield improved photovoltaic performance by controlling directional current flow through a bulk preferentially aligned thin-film.
Figure 1. (a) Molecular structures for the conjugated polymer films PCDTPT (poly[[1,2,5]thiadiazolo[3,4-c]pyridine-4,7-diyl(4,4-dihexadecyl-4Hcyclopenta[2,1-b:3,4-b’]dithiophene-2,6-diyl][1,2,5]thiadiazolo[3,4-c]pyridine-7,4-diyl(4,4-dihexadecyl-4H-cyclopenta[2,1-b:3,4-b’]dithiophene-2,6-diyl)] (1) and P3HT (poly-3-hexylthiophene (2) studied here. (b) Prototypical UV-vis-NIR absorption spectra for the toluene dispersion (yellow) and dropcast film (green) PCDTPT and P3HT film (blue) samples. 400 nm and 800 nm excitation wavelengths are displayed to indicate the approximate locations within each absorption band where photoexcitation occurs in this work.

Electronic absorbance (UV-vis-NIR) spectra are shown in Figure 1b to highlight the prototypical absorption profiles of PCDTPT and P3HT in films and a PCDTPT dispersion in toluene. Unlike P3HT, PCDTPT is largely unimpacted by solvatochromism but does show significant spectral broadening as a film, suggesting increased disorder in the film. PCDTPT is characterized by two primary absorptive features: (1) a low lying internal charge transfer transition centered at 900 nm and (2) a higher-lying band centered at 450 nm attributed to the excitation of π-electrons (π-π*) within the bridged bithiophene moieties. The 900 nm dipole is aligned along the polymer backbone for a similar polymer, and assuming that the (450 nm) bridged bithiophene transition is delocalized it should exhibit similar alignment. From here, Kasha’s Rule (if maintained) would suggest that excitation of either band should lead to similar if not identical charge separated states. When employing Equation 3 to calculate the complex conductivity, the effective carrier mass (m*) is taken to be 0.106 m_e for PCDTPT and
0.25 m$_e$ for P3HT$^{49}$ as determined in previous studies (though literature values for P3HT range between 0.12 m$_e$ and 1.7 m$_e$).  

Aligned films of PCDTPT can be produced by tunnel drying$^{38}$ or blade coating$^{33}$ onto optionally nanostructured (grooved) THz-transmissive substrates. Herein, PCDTPT alignment refers to the direction along the polymer alignment axis, i.e., the direction of polymer backbone propagation. Blading variations lead to differences in surface thickness, morphology, and device performance for P3HT films, but are less impactful in PCDTPT and beyond the scope of this work.$^{51}$ PCDTPT and P3HT can also be prepared as dropcast samples or suspended in solvent to obtain varying degrees of isotropically distributed polymer samples and, in the case of solvent dispersions, increasingly isolated transients and carriers. Solvating PCDTPT in various organic solvents, including toluene, has been shown to disrupt ordering sufficiently well to prevent the formation of crystalline domains between the relatively disordered polymer microaggregates.$^{52}$ All three types of PCDTPT organization provide slightly different perspectives on local order/morphology, ranging from near uniaxial alignment to randomly arranged sub-domains to a disordered and electronically isolated dispersion.  

To outline this article, we first present time and frequency-dependent analyses of photoconduction in conjugated polymers PCDTPT and P3HT. Charge carrier mobilities and generation yields are extracted for each sample as a function of alignment to anisotropic excitation using non-contact TRTS. We show that anisotropic conduction occurs within these conjugated polymeric networks and interpret the observed anisotropies for practical implications. We then contrast these anisotropic datasets to films with nominally isotropic morphologies to highlight the strongly enhanced directional conduction behavior of deliberately grooved and bladed film structures. In addition to the near-isotropic films, we report the first known observation of transient conduction in dispersed PCDTPT, occurring with the aid of a rigidly aligned backbone or intermolecular interactions within disordered microaggregates. To our knowledge, a similar magnitude of charge conduction between a conjugated polymer dispersion in solution and its
corresponding film has not previously been observed for other dispersed polymer systems. Finally, we describe how metrics of charge carrier population (through transient near-IR absorption) and conduction are contrasted to differentiate between their population/positioning and net motion.

EXPERIMENTAL METHODS

Sample Preparation

PCDTPT (MW 72 kDa and dispersivity index of 2.5) and regioregular (RR)-P3HT (MW = 50 kDa to 100 kDa, > 90 % RR) were obtained from 1-Material and Millipore/Sigma-Aldrich,\textsuperscript{53} respectively, and used as received. All substrates were THz-transparent amorphous quartz (GM-Associates GM 7500-01).\textsuperscript{53} Two PCDTPT films were prepared \textit{via} blading-coating. One was prepared by blading at low speed (0.2 mm/s perpendicular to etched = 2 nm deep grooves) and labeled (G)-PCDTPT. The combined ordering effects of the grooves (bottom, parallel polymer guidance) and slow blading speed (top, perpendicular to the blade/parallel to the groove guidance) produce a PCDTPT film with ca. linearly anisotropic morphology throughout. A second sample was bladed at 100 mm/s on an ungrooved substrate and labeled (UG)-PCDTPT. Additional information is included in the SI (Figure S1) while other details of the blading procedure have been discussed previously.\textsuperscript{33}

A third film was prepared by dropcasting 20 µL of a 4 mg/mL PCDTPT in dichlorobenzene and chloroform solution (1:3 %v/v) onto a substrate, labeled (DPC)-PCDTPT. This film showed less anisotropic steady state absorption than either bladed sample and is the closest film that approximates an isotropic sample; ratios of the steady-state 800 nm absorbance along the highest absorption axis relative to the orthogonal direction’s absorption were 2.45, 1.65, and 1.37 for (G), (UG), and (DPC), respectively. The three samples facilitate comparison of a reasonably well-aligned throughout (G), less uniformly ordered (UG), and an intended near-isotropic (DPC) set of films. These sample thicknesses were determined by ellipsometry to be ≈ 250 nm thick, with specific thicknesses, optical absorptions at
800 nm, and penetration depths described in the SI in Table S1. Each surface of similarly prepared (G) and (UG) samples were previously evaluated using X-ray diffraction (with extensive characterization).\textsuperscript{33} Integrated layer alignment was assessed from in-situ photoexcitation pulse absorption and steady-state polarized absorption spectra. Example polarized absorption spectra for (G) and (DPC) are included in the Supporting Information (SI) as Figure S2 and reflect the degree of anisotropic polymer arrangement in the film.

A liquid phase dispersion, (S)-PCDTPT, was prepared by dissolving PCDTPT in toluene to a concentration of $\approx 0.2$ mg/mL and was studied in a 1 mm pathlength quartz cell. RR-P3HT was prepared as a thicker ($> 500$ nm), isotropic dropcast film cast from solution in chloroform ($> 5$ mg/mL). No appreciable absorption anisotropy was obtained by polarized 800 nm beams transmitted through (S)-PCDTPT or for 400 nm through P3HT. Each film studied here was greater than or approximately double the thickness of the spectroscopic excitation penetration depth, and the shorter of these depths was used as the interaction volume for determining the carrier number density, $\Delta N$ (see SI, Table S1). The data presented here were collected using conditions with reduced excitation intensity such that the sample showed no appreciable degradation from laser (or air) exposure over the course of the time-resolved measurements and ca. linear THz probe response. UV-vis-NIR spectra were collected using a Perkin Elmer, Lambda 2 UV/VIS spectrometer.\textsuperscript{53}

\textit{Ultrafast Terahertz (TRTS/TDS) Apparatus}

Time-resolved THz spectroscopy (TRTS) measurements were performed as in previous experiments\textsuperscript{13,39} based on the laser system diagram shown in Figure 2. A more complete description of the spectroscopic set-up is provided in the SI. Briefly, to collect time-dependent, frequency-resolved THz spectra (TDS), probe pulses were iteratively blocked with an optical chopper and the probe-gate optical delay swept using a translation stage. Signal voltages readout from the difference of dual balanced
photodiodes were detected by a lock-in amplifier (Stanford SRS-830). Monitoring the polarization-sensitive electro-optic transmission of a weak gate pulse through a ZnTe <110> detector crystal permitted extracting the full time-dependent electric field waveform of the probe pulse. Fast Fourier transform (FFT) provided the frequency-dependent and complex unexcited spectrum, \( \hat{E}_0 \). Using the optical chopper to instead iteratively block the photoexcitation pump pulse at a fixed pump-probe time delay (TRTS-TDS) produced the frequency-dependent change in this spectrum due to photoexcitation, \( \Delta \hat{E} \). Alternatively, fixing the probe-gate delay where the maximum probe electric field \( \hat{E}_0 \) occurs, chopping the pump, and sweeping the pump delay yielded the overall kinetics of photoinduced sample conductivity through integrated TRTS measurements. Splitting and scaling the detector signals between two lock-in amplifiers set to the frequencies of each optical chopper separately (e.g., 1a and 1b in Figure 2) allowed for simultaneous collection of \( \Delta \hat{E} \) and \( \hat{E}_0 \) signals in TRTS-TDS or integrated TRTS measurements.

**Figure 2.** Schematic diagram of the TDS/TRTS Ultrafast THz apparatus with optical components labeled according to the included key.

All (G) and (UG) results were normalized to excitation fluences of 1 \( \mu J/cm^2 \) for 800 nm and 2 \( \mu J/cm^2 \) for 400 nm (unless stated otherwise) to maintain a consistent input photon count. Additionally, results were normalized to a peak ground state \( \hat{E}_0 \) signal of 1 mV. All films were photoexcited through the back
of the film unless indicated otherwise to be incident with the grooves and the film surface less prone to photooxidization. Differences in sample absorption at different pump polarization orientations and surface Fresnel losses were normalized and corrected. Example data collected for the time-dependent interference of the probe THz with the gate pulse and the resulting FFT yielding the frequency-resolved spectrum, are included as Figures S3a and S3b in the SI.

Consecutive measurements were collected for the same spot of each sample under four polarization conditions highlighted in Figure 3 in order to separate excitation anisotropy from the anisotropic THz response. The pump polarization was controlled by rotating a half-wave plate; the sample itself was rotated to alter the blading direction relative to both the pump and probe polarizations without altering the spatial overlap of the pump and probe. The THz probe was focused using parabolic mirrors to a spot size of ≈1.5 mm diameter and overlapped entirely with the 3 mm diameter pump beam.

Figure 3. Orientations of pump (orange) and THz probe (red) beam polarizations relative to the blading direction (green) for four polarization configurations. Specifically, parallel (a, b) and perpendicular (c, d) pump:blade (Pu:B in figure) and parallel (a, d) and perpendicular (b, c) probe:blade (Pr:B) directionalities are illustrated.

All TRTS data processing and error analysis were accomplished using homebuilt data analysis algorithms and specific details are provided in the SI. All reported error bars and numerical errors are
included as 95 % confidence intervals (CIs), which span approximately two standard deviations. Errors were determined by numerical averaging or applying nonlinear error modeling to parameters obtained from nonlinear least squares regressions, as detailed in the SI.55

Ultrafast Transient Absorption Set-up

Transient absorption (TA) measurements were conducted using 800 nm, 100 fs FWHM excitation pulses and a broadband supercontinuum probe. The excitation fluence was \( \approx 0.4 \text{ mJ/cm}^2 \), approximately 30 % of the fluence used for conduction measurements. Pump-induced change in the absorption at 1200 (+/- 10) nm from the probe was measured, which is primarily sensitive to the oxidized PCDTPT state, the most readily observed transient state of interest.44 For the (DPC) film, the birefringence of the polymer layer was found to scramble the polarization ratio of the transmitted probe from an extinction ratio of > 70:1 to 12:1. We determined that the error in the resulting polarization anisotropy from this mixing of parallel and perpendicular polarizations was < 0.03 (assuming uniform pump excitation throughout), and no explicit correction was applied in the analysis. TA traces were processed using similar kinetic models to the TRTS data and details are provided in the SI.

RESULTS AND DISCUSSION

Polymer Conduction Anisotropies

Normalized 800 nm pump and THz probe TRTS decays are shown as a function of pump-probe delay in Figure 4a for the (G)-PCDTPT film. All four pump:blade and probe:blade polarization configurations are shown to illustrate their relative (normalized) signal magnitudes. Each set of kinetic data was modeled as a bi-exponential decay and constant offset convoluted with a Gaussian instrument response function which fits the observed trends well. The inset depicts the slight differences in offset/constant tail fits through each decay at long time delays. Figure 4b displays the signal comparison between parallel (red)
and perpendicular (blue) pump:probe geometries from 400 nm excitation of the ostensibly isotropic, dropcast P3HT film. The observed conduction anisotropy in this P3HT sample (the difference between red and blue traces of Figure 4b) is much weaker than that of pump:probe anisotropy observed perpendicular to the blading direction of (G) (green compared to purple of Figure 4a).

![Figure 4](image.png)

**Figure 4.** Integrated TRTS illustrated for (a) (G)-PCDTPT and (b) P3HT films for different excitation and probe polarizations. The key displays (a) pump:blade / probe:blade and (b) pump:probe polarization configurations. The inset in (a) reveals the long time (tail) traces of smooth models fit through each dataset. PCDTPT TRTS plots were normalized to excitation via a 1.04 mJ/cm², 800 nm pulse. The time delay axis for each plot is linear from -1 ps to 1 ps and logarithmic beyond 1 ps.

PCDTPT conduction anisotropies were determined by applying Equation 1b to the maximum peak of each signal (Δt = 300 fs to 500 fs, “peak”) and the average of the longer time delay data points (Δt > 10 ps, “tail”) to represent the instantaneous and thermalized conductivities, respectively. Owing to greater signal intensities, peak conduction and anisotropies are more accurately determined than tail equivalents and are useful in comparing initial charge carrier generation, recombination, and alignment mechanisms. Tail conduction and anisotropies represent the charge conductive processes occurring towards a thermalized and DC-like limit more relevant to the performance of optoelectronic devices.

(G) and (UG) samples were photoexcited using 800 nm or 400 nm pump pulses across three sets of analyses. The first and second involved interrogating (G) and (UG) as a function of polarization
configuration and pump wavelength. The polarization anisotropies \( r(t)'s \) determined for (G) are displayed as bar charts in Figure 5, with anisotropic values determined for the reference P3HT film excited at 400 nm included the final set of bars. Most of the parallel discussion for sample (UG) is shown Figure S4 of the SI, as it showed qualitatively similar (albeit directionally opposite) results as for (G). (UG) exhibits less uniformly anisotropic layering compared to (G) due to random sub-domain formation during solvent evaporation. Briefly, the third analysis compared 800 nm excitation of the top and bottom surfaces of (UG) via excitation of the front and back of the film (Figure S5 of the SI) to differentiate polymer ordering at each surface and as a function of layer depth. This revealed anisotropic discrepancies owing to preferential charge pair formation at either surface incident to the photoexcitation pulse. Plots comparing (UG) anisotropies and corresponding tabular values for peak and tail anisotropies associated with all (G), (UG), and P3HT data may be found in the SI as Figures S4 and S5 and Tables S2a and S2b.

**Figure 5.** Conduction anisotropies calculated for (G)-PCDTPT and P3HT films extracted from the photoexcited peak (red/yellow bars) and tail (green/purple bars) for each conduction signal. The bottom axes labels indicate the orientation of the excitation polarization to the blading direction (pump:blade) and excitation wavelength (nm). All error bars represent 95 % CIs.

The anisotropies in Figure 5 illustrate preferential charge conduction perpendicular to the blading direction of (G)-PCDTPT, even correcting for anisotropic absorbed photoexcitation. (G) displays a
positive anisotropy for excitation perpendicular to the blading direction and interestingly, a negative anisotropy for parallel excitation. This occurs for both the photoconductive peak and the long-lived tail signatures. Recall, \( r(t) \) measured perpendicular to the blading direction in (G) is synonymous with being parallel to the inlaid grooves and polymer backbone orientation along the film’s bottom, and similarly aligned top, surfaces. Comparing back and front surface excitation of (UG) (SI Figure S5) shows unequal and depth dependent polymer alignment and notably more positive tail conduction anisotropy when exciting from the back surface.

Excitation via 400 nm light exhibits qualitatively similar anisotropies to 800 nm excitation. This occurs from internal conversion of the transient state excited at 400 nm (i.e., the \( \pi-\pi^* \) transition along the bithiophene ring moiety) into polarons alternatively formed directly through 800 nm excitation of the (bithiophene donor to thiadiazolo-pyridine acceptor) charge transfer band. Excitation at 800 nm typically incurs more positive anisotropies at the peak conduction responses than observed in the tails (including across unshown datasets with \( \perp/800 \) in Figure 5 as an exception), while 400 nm excitation consistently yields more negative peak than tail anisotropies. Additional underlying absorption features that have dipoles unaligned to the two transitions studied here (e.g., direct absorption by the acceptor and additional energy dissipation following 400 nm excitation) may explain some of the anisotropic difference between excitation wavelengths. Despite minor discrepancies, the geometric dependencies are qualitatively alike and consistent with a common charge separated state and functionally similar dipole orientation arising from either excitation.

Figure 5 reveals that compared to the (G) PCDTPT film, dropcast P3HT exhibits comparatively low 3D conduction anisotropy (e.g., 0.1 at the photoconductive peak and 0.17 at the long time-delay tail) which align well with anisotropies seen experimentally in population metrics, i.e., fluorescence.\(^56\) Other methods of straining P3HT films or aligning the polymer into thin channels have been shown to dramatically increase this level of anisotropy.\(^27,57\) Comparison of dropcast P3HT to (G) allows for the
anisotropic effects of embedding polarization through photoexcitation to be considered more independently from those stemming from sample morphology. Quantitative comparison can, however, be confounded by details concerning 2D vs 3D conductive networks and the charge transfer properties of P3HT (largely overlooked for this study). We now turn to discussing implications of the persistent anisotropy and considering their origin in terms of polaron population dynamics and local mobility.

If directional excitation of a 2D conductive system, \((G)\), did not influence its polarization anisotropy then one would expect perpendicularly polarized photoexcitation to yield the negative value for the anisotropy measured for parallel excitation. Instead these magnitudes vary depending on the pump polarization for both the peak and tail conductivities and hinge on how the photoexcitation dipole is aligned along or orthogonal to the anisotropic sample morphology. One can determine the relative degree of static sample alignment to lead to each of the observed anisotropies, though the persistence and prevalence of unequal anisotropies when normalizing for the relative absorbance of the excitation source is most noteworthy. These varying anisotropies hint that the photophysical nature of charge generation and morphological preference for conduction are not synonymous, warranting a more in-depth anisotropic analysis to clarify their dependencies.

**Frequency-Dependent Analysis**

To differentiate between competing factors responsible for the observed anisotropies, frequency \((v)\)-dependent TRTS data were collected at fixed pump-probe time delays. Subsequent spectral analysis and modeling permitted extraction of carrier conductivity, yields, and total charge (electron + hole) mobility. As described in the Experimental section, the time-resolved response \(\Delta \hat{E}\) was evaluated at a fixed pump-probe time delay with respect to the unexcited probe response, \(\hat{E}_0\), FFT was applied, and the sample’s complex conductivity \((\hat{\sigma}(\omega))\) was extracted using Equation 2. Frequency dependent data and fits using Equation 3 for the peak photoconductive signals for \((G)\)-PCDTPT are shown in Figure 6a.
The corresponding frequency-dependent response for the less conductive, dropcast P3HT film is included as Figure 6b and can be related to a previous report.\textsuperscript{15}

\textbf{Figure 6.} Peak frequency-dependent conductivity (points) and Drude-Smith model fits (lines) for (a) perpendicular pump:blade (G)-PCDTPT sample collected using 1.7 mJ/cm\textsuperscript{2}, 800 nm excitation and (b) P3HT using 0.22 mJ/cm\textsuperscript{2}, 400 nm excitation. (a) depicts the frequency dependence of the anisotropy trends observed in the third red bar and (b) the yellow bar of Figure 5. Blue vs. red points/lines indicate parallel (\parallel/\parallel) and perpendicular (\parallel/\perp) pump:probe polarizations and closed dots/solid lines vs. open squares/dashed lines indicate real and imaginary conductivities, respectively.

The real and imaginary spectral data were simultaneously fit between lower (0.25 THz to 0.5 THz) and upper (2 THz to 2.25 THz) frequency bounds by the Drude-Smith model. A nonlinear least squares regression using the Levenburg-Marquardt fitting algorithm yielded optimal parameters for each data set, which are presented with their 95 % CIs in Table S3 of the SI. Corresponding correlation coefficient ($r^2$) values are greater than 0.7, though some datasets (parallel data in Figure 6a) show trends that appear inadequately fit. The poor fits may be attributed to a combination of inconsistent pump-probe overlap for low frequency data via a spatially chirped probe, weighting to central frequencies with higher probe fields, and nonconforming curvature in the real part of the high frequency region. The latter cannot be fit as the product of two sub-populations of charge conductors or with corrections (e.g. Cole-Cole or Cole-Davidson) applied to the model.\textsuperscript{58} In spite of this, the lowest-frequency data points do
not significantly affect the Drude-Smith model fits, the imaginary portion of the high frequency data is well fit (simultaneously with the real part) and the model proves very effective in fitting (DPC), (S), and P3HT samples ($r^2 > 0.9$). Thus, the parameters determined from the Drude-Smith model are qualitatively applicable despite limited deficiencies in representing certain (G) and (UG) datasets.

**Evaluating Relative Charge Carrier Mobility and Efficiency**

The parameters $\Delta N$ and $\tau$ (mean scattering time, fs) were determined from fitting with the Drude-Smith model (Equation 3) and used to extract the total charge carrier mobility, $\mu_P$, with Equation 4a. Equation S4 in the SI may alternatively be used to determine the limiting low frequency conductivity$^{13}$ and agrees both qualitatively with relative orderings and quantitatively with Equation 4a to within 25%. We used Equations 4a and 4b to determine mobility values based on the precedent previously set for P3HT with additional information provided in the SI.$^{15}$ Mobility determined (by either equation) is included for each dataset in Tables S4 and S5 of the SI. Charge carrier generation efficiency, $\Phi_{\text{eff}}$, was calculated as the ratio of the extracted charge carrier density $\Delta N$ (charge pairs/cm$^3$) to the empirically measured photon density (photons/cm$^3$) absorbed for each sample configuration and included in Table S4. $\mu$ and $\Phi_{\text{eff}}$ provide metrics for the total carrier mobility and how many charges are generated along the selected probe polarization direction by polarized photoexcitation, respectively. These conditions and values help determine the nature of anisotropic conduction. Figure 7 shows the calculated $\mu_P$, $\mu_{\text{PDS}}$, and $\Phi_{\text{eff}}$ for (G)-PCDTP (7a) and P3HT (7b) film samples.
Figure 7. Extracted peak mobility (\(\mu_p\), red/purple), peak Drude-Smith mobility (\(\mu_{DPS}\), grey) and charge generation efficiencies (\(\Phi_{\text{eff}}\), green/yellow) for (a) 800 nm excitation of (G)-PCDTPT and (b) 400 nm excitation of isotropic P3HT films. Pump:blade and probe:blade (a) or pump:probe (b) orientations are indicated by the abscissa labels (|| = parallel and \(\perp\) = perpendicular).

The TRTS \(\Delta E\) signal measured for each polarization configuration scales as the product of \(\mu_p\) and \(\Phi_{\text{eff}}\). Each photoconductive peak anisotropy measured and shown in Figure 5 is equivalent to calculating an anisotropy (Equations 1a and 1b) from the \((\mu_p \times \Phi_{\text{eff}})\) products of the parallel and perpendicular probe:blade values extracted for each pump:blade configuration. For example, the anisotropy determined from the product of the red and green bars of the first column (\(S_{||}\) in Equation 1b) to the product of those in the second column (\(S_{\perp}\) in Figure 7a yields the slightly negative peak anisotropy seen as the first column (red) in Figure 5. In this way, the relative roles of the “velocity” \(\mu\) and effective “number density” \(\Phi_{\text{eff}}\) of the charge carriers can be isolated to explain the trends observed in the overall conduction anisotropies.

Extracted mobility values (from conduction spectra in Figure 7a) for the films are reported for the conduction peak of each sample. The mobility along the grooves is found to be measurably higher than perpendicular to the grooves. This improvement in mobility is statistically significant (see statistical analysis in Table S7 of the SI) though modest compared with discrepancies seen from transistor comparisons.\(^{33}\) This highlights the primary and most intuitive reason why conduction anisotropies favor...
propagation along the length of the polymer; charges traversing a material surface more rapidly will exhibit higher conduction signals, in agreement with the directionality of FET conduction results observed previously.\textsuperscript{27,33} We conclude that carrier mobility is greater along the polymer backbones due to anisotropic alignment of their propagation directions with anisotropic conduction aided by the near linear polymer orientation over the finite (and short) charge transfer length scale accessible by TRTS.\textsuperscript{15}

Discrepancies between the magnitudes of the measured conduction anisotropies indicate that mobility is not the only factor impacting directional conductivity. Specifically illustrated in Figure 7, the preferential conduction trends seen in $\mu_p$ (red) do not consistently agree with those predicted by $\Phi_{\text{eff}}$ (green). For (G), the parallel pump:probe polarization configurations (those with the same orientation relative to the blading direction, i.e., columns 1 and 3) exhibit higher $\Phi_{\text{eff}}$ than their perpendicular counterparts (columns 2 and 4). The uneven ratios between different probe direction spectra reveal greater $\Phi_{\text{eff}}$ anisotropy resulting from excitation along the grooves than across them. Morphological evidence of the grooved/bladed alignment funneling charge carriers can be seen by $\approx$ twice as many carriers being produced per absorbed quanta for perpendicular pump:blade and parallel probe:blade alignment as the opposite configuration (parallel and perpendicular, respectively) despite equivalent pump:probe alignment. The more anisotropic charge pair yield from parallel pump:blade suggests that significantly more polarons (i.e. associated dipoles) are created when the conduction channels are aligned to the excitation source, even when corrected for pump fluence and sample absorptivity. These derivations suggest that $\mu_p$ and $\Phi_{\text{eff}}$ depend on both the sample morphology and dipole orientation of the photoexcitation and probing pulses but also demonstrate that the primary determining factors for $\mu_p$ and $\Phi_{\text{eff}}$ are the sample morphology and dipole orientation, respectively.

Overall, PCDTPT produces substantially higher photoconductive signals than P3HT with comparatively higher mobility and lower charge generation efficiency, though these largely result from differences in carrier effective mass between the polymers. The lower effective mass for polarons in PCDTPT than
P3HT is likely a result of its donor-acceptor copolymer structure and less resistance to movement of the polaron along individual segments of the polymer. Frequency-dependent analysis of P3HT conduction shown in Figure 7b reinforces these dependencies. For a dropcast, randomized film with isotropic ordering and absorbance (having < 3 % variability with polarization), during the photoconductive peak signal the $\mu_p$ is higher and $\Phi_{\text{eff}}$ is lower for the parallel pump:probe polarization configuration compared to perpendicular. The anisotropic dependence of the $\mu_p$ of P3HT supports favorable mobility along the polymer backbone, though the opposite anisotropic trend in $\Phi_{\text{eff}}$ favors perpendicular conduction. These offsetting factors mitigate the observed conduction anisotropy resulting in a low initial anisotropy of 0.1 (Figure 5). The anisotropic dependence of $\Phi_{\text{eff}}$ decreases with time towards the thermally relaxed limit though uncertainty in modeling the weak P3HT tail data hinders a more quantitative determination.

Mobility values ($\mu_{\text{PDS}}$) extracted from Drude-Smith fitting shown as grey bars in Figure 7 are noteworthy as well. In PCDTPT they decrease to about one-fourth of the average peak mobility, and since the relative magnitudes between polarization configurations do not substantially change, many of the same qualitative conclusions discussed previously still apply. For P3HT, however, the very different $c_1$ backscattering parameters (Table S3) leads to a reversal of the anisotropic dependence of mobility ($\mu_{\text{PDS}}$ vs. $\mu_p$), implying that long range charge transfer may be preferentially intermolecular. Namely, parallel $\mu_{\text{PDS}}$ becomes less than perpendicular $\mu_{\text{PDS}}$ whereby both $\Phi_{\text{eff}}$ and $\mu_{\text{PDS}}$ are higher for perpendicular excitation when considering delocalized interactions (at low THz). The anisotropy calculated from $\mu_{\text{PDS}} \cdot \Phi_{\text{eff}}$ is $\approx -0.17$ ($\approx 0.1$ from $\mu_p \cdot \Phi_{\text{eff}}$) and no longer agrees with the anisotropy determined through integrated TRTS values shown in Figure 5. We conclude that this arises from disproportionately lower frequency photoconduction (Figure 6b) for perpendicular compared to parallel pump:probe orientation and suggests more perpendicular conduction (relative to the original excitation dipole) over long distances. By contrast, PCDTPT shows no noteworthy trend of this nature.
We avoid placing emphasis on quantified differences in $\mu$ and $\Phi_{\text{eff}}$ between or amongst polymer results as $m^*$ for each polymer may vary for different local polymer configurations (dihedral flexibility)\(^{49}\) and $m^*$ values are slightly different among reports.\(^{48,49}\) The determined mobility also deviates substantially from microwave\(^{59}\) and thin-film transistor\(^{33}\) measurements (by orders of magnitude) as alluded to previously and exemplified by comparisons to $\mu_{\text{PDS}}$.\(^{15}\) Variations attributed to $\Phi_{\text{eff}}$ and reflected in $\mu_{\text{PDS}}$ for P3HT may arise from directionally non-uniform $m^*$ of the generated charge carriers within a given intermolecular polymer domain. This Drude-Smith model parameter is closely tied to the reported carrier $\Delta N$ via Equation 3, or since $\Phi_{\text{eff}}$ and $m^*$ are not determined independently, $m^*$ and $\Delta N$ cannot be disentangled. It is feasible that the carriers generated along a parallel pump:probe direction (or grooves) in (G) have a lower effective mass than those generated orthogonal to photoexcitation (or grooves). This implies that despite the morphological impact on mobilities (i.e., charge motion velocities), the potential energy landscape around and molecular nature of charge carriers differentiates between the friction (i.e., resistance) of motion in certain directions. This resistive element would impact the likelihood of charges traveling in different directions and would heavily depend on the geometries of the molecular orbitals involved in the polarized excited state and intermolecular/morphological environment. Comparing to classic charge conduction, this would be analogous to relating mobilities to molecular currents ($\mu \rightarrow I$), charge carrier generation efficiencies to a voltage ($\Delta N \rightarrow V$), and, interchangeably, effective mass to a resistance ($1/m^* \rightarrow 1/R$). Differences in the harmonic mean of the involved charge carriers, i.e., sub-populations of electrons and holes, as a function of morphology and anisotropic photoexcitation could be responsible for differences attributed to total number of generated charge carriers, $\Delta N$. While we acknowledge this explanation to be plausible, it is not explored further in this work.

*Comparison between Isotropic Films (DPC) and Dispersion (S) Samples*
PCDTPT is known to conduct charge primarily through intramolecular channels and exhibit large intramolecular delocalization similar to other donor-acceptor copolymers.\textsuperscript{16,60} However, the dependence of surface charge conduction on local sample morphology is not understood. Additional analyses were conducted to contrast the frequency-dependent spectra for both the peak and tail photoconductive signals of the more isotropic, dropcast PCDTPT film (DPC) and completely isotropic dispersion in nonpolar toluene (S) samples. These provide more comprehensive insight into the effect of local ordering on charge carrier motion and mobility.\textsuperscript{61} Frequency-dependent traces of the real and imaginary conductivities for (DPC) and (S) are shown in Figures 8a and 8b, respectively.

![Figure 8](image)

**Figure 8.** Real (circles/solid lines) and imaginary (squares/dashed lines) conductivity for the peak (blue) and long delay time tail (red) signatures for (a) the near-isotropic PCDTPT film (DPC) and (b) the PCDTPT/toluene dispersion (S). Spectra were collected using 800 nm excitation with fluences of (a) 1.7 mJ/cm\(^2\) and (b) 0.98 mJ/cm\(^2\). The DC-tail conductivities are multiplied by 15 to permit visual comparison to peak data. (S) conductivity is calculated using a film equivalent thickness for the absorption observed through the 1 mm pathlength cell.

Qualitatively, the photoconductive signal drops by a factor of \(\approx 20\) when comparing the photoinduced peak to the thermalized tail, though the remaining conductivity persists out to the longest time delay measured (\(\approx 200\) ps; not shown). The change in real vs. imaginary conductivity relative magnitudes suggests an increase in localization\textsuperscript{\textsuperscript{62}} and trapping of charges\textsuperscript{\textsuperscript{63}} and a decrease in probability of charge
transfer upon each scattering event at longer time delays compared to initially hot polarons. Changes in the curvature of the frequency dependence with time signify changes in scattering time. Short scattering times reflect the rapid, localized interactions that charges have at the fringes of their polaron domains while the magnitude of the scattering time can indicate the relative size of and ease with which a charge can move across its polaron domain. Table 1 highlights the fit parameters extracted from the results presented in Figure 8 and concisely reflect differences between (DPC) and (S). Drude-Smith model pre-factors \( \Delta N \cdot q^2 m^* \) can be compared between peak and tail data of each sample; the (S) photoconductive signal was modeled to emulate a of a film of equivalent absorption/thickness as (DPC), permitting qualitative pre-factor comparison despite vast differences in sample thicknesses and polymer densities.

**Table 1.** Conductivity pre-factors, scattering times, and backscattering parameters derived from frequency-dependent conductivity data shown in Figure 8.

| Parameter          | (DPC) Peak /
|                   | (95 % CI) | (DPC) Tail
|                   | (95 % CI) | (S) Peak
|                   | (95 % CI) | (S) Tail
<table>
<thead>
<tr>
<th>(s(^{-1}), S/m(\cdot)ps)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta N \cdot q^2 m^* )</td>
<td>20.9 ( (15.0 – 39.2) )</td>
<td>2.5 ( (0.9 – 54.2) )</td>
<td>4.6 ( (3.7 – 6.0) )</td>
<td>2.3 ( (0.5 – 70.2) )</td>
</tr>
<tr>
<td>( \tau ) (fs)</td>
<td>22.1 ( (12.3 – 32.3) )</td>
<td>16 ( (3 – 27) )</td>
<td>54.7 ( (46 – 63.4) )</td>
<td>18 ( (2 – 40) )</td>
</tr>
<tr>
<td>( c_1 ) (-1 (-\leftrightarrow) 0)</td>
<td>-0.757 ( (-0.811 – -0.718) )</td>
<td>-0.946 ( (-1 – -0.891) )</td>
<td>-0.905 ( (-0.942 – -0.868) )</td>
<td>-0.962 ( (-1 – -0.932) )</td>
</tr>
</tbody>
</table>

Two stark differences arise between the fit parameters of the peak film and dispersion phase data. First, the scattering time for (DPC) is \( \approx 2.5 \) times shorter than for (S), (i.e., \( \tau_{(S)} = 2.5 \tau_{(DPC)} \)), implying that scattering events occur less frequently for electronically isolated strands. Second, the backscattering
parameter \( (c_1) \) for the film is significantly more negative towards the full “backscattering” limit of -1 for (S) than (DPC), \( (c_{1(S)} < c_{1(DPC)}) \). This indicates that a larger proportion of charges in the film “forward-scatter” toward another site rather than “backscatter” or remain confined within the original boundaries of the associated polaron. It is important to note that forward- and back-scattering do not indicate the length or absolute directionality of each scattering event, i.e., forward-scattering could represent motion of the charge carrier away from or towards its origin at each finite scattering step. Though differences in \( \tau \) and \( c_1 \) complement one another, they manifest independently and visually as the curvature of the real frequencies and curvature/negative offset of the imaginary frequencies, respectively (e.g., the distances between the imaginary conductivities and zero in Figure 8a).

Figure 9 reflects the corresponding comparisons of \( \mu_P \), (scaled) \( \mu_{PDS} \), and \( \Phi_{eff} \) of (S) and (DPC) akin to that seen for (G) and P3HT in Figure 7. Unlike the dropcast, isotropic P3HT film most of the observed conduction anisotropies for (DPC) and (S) occur as a result of differences in \( \Phi_{eff} \) rather than \( \mu \), though this isn’t too different from (G). The dramatic change in magnitude between \( \mu_P \) and \( \mu_{PDS} \) for (S) reflects a significantly more negative backscattering parameter \( (c_1) \) compared to (DPC) and other samples. Analysis for tail mobilities \( (\mu_T \text{ and } \mu_{TDS}) \) was attempted for these samples and is shown in the SI as Figure S6.

![Figure 9](image)

**Figure 9.** Extracted peak mobilities \( (\mu_P, \text{ blue}) \), Drude-Smith mobilities \( (\mu_{PDS}, \text{ grey}) \) and charge generation efficiencies \( (\Phi_{eff}, \text{ brown}) \) for 800 nm excitation of (S)- and (DPC)-PCDTPT samples. The samples and
pump:probe orientations are indicated by the abscissa labels (|| = parallel and ⊥ = perpendicular). $\mu_{PDS}$ is multiplied by a factor of 4 for clarity.

Turning to the tail data $\tau$ and $c_1$ fit parameters (Table 1), (DPC) and (S) converge towards similar values at late time delays, also apparent from the similarities of the tail (red) traces between Figures 8a and 8b. This convergence indicates that following initial recombination, energy dissipation processes, and trapping (largely within the first few picoseconds) the conductive polarons behave similarly whether residing on electronically uncoupled or isolated strands immersed in a dielectric solvent compared with a two-dimensional conductive network coupled to surrounding polymer. Despite convergence of $\Delta N \cdot q^2 m^* - 1$, comparison of absolute conduction is difficult given the difference in sample density and heterogeneous nature of the polymer. Also, the cumulative behavior (projection onto the longer time/distance scales) may be vastly different, as slight differences in rapid $\approx 20$ fs scattering events occurring throughout the remaining polaron lifetime (greater than a nanosecond timescale) can have a large impact on net charge carrier motion. Overall, charge carrier behavior is comparable in either environment in the thermally relaxed, long time limit.

Upon photoexcitation, intermolecular orientation and stabilization promotes intrachain charge motion in the film (weaker in the liquid phase sample) and manifests as more rapid scattering events with a greater proclivity for discrete motion along a given strand. Charge formation and propagation in (S) will also be impacted by the solvent’s low dielectric constant, which likely destabilizes polarons relative to singlet excitons when compared with a film environment. This degree of freedom went unexplored in this study owing to degradation of the photoexcited sample in chlorinated solvents and limited THz transmission scaling with solvent polarity. Thermal dissipation may also play a varying role in each, specifically because the (DPC) sample absorbs light in a significantly smaller active volume than (S) leading to a much greater potential for local heating. P3HT:PCBM solar cells exhibit decreasing open-circuit voltages for constant fill factors and external quantum efficiencies with increasing temperature.
near room temperature.\textsuperscript{64} We anticipate that local heating would drive the system towards more frequent scattering (shorter $\tau$) and lower voltages (lower $\Delta N$) which do not directly correlate with the observed sample differences. Follow-on studies could be conducted at lower fluences and different temperatures to isolate this potential effect. Lastly, the dispersion of a donor-acceptor conjugated polymer (PCDTPT) yielding comparable TRTS signals to an analogously absorptive film is significant. Many other polymer dispersions examined to date, such as P3HT (as isolated strands or nanorods not included in this paper) do not produce any measurable photoconductivity response. Other polymers, such as MEH-PPV, do show isolated, solvated conduction but with far less conductivity than in films,\textsuperscript{61} while PCDTPT produces comparable conductivity under either circumstance.

\textit{Relation between Polarized Photoconductivity and Transient Absorption}

Finally, to distinguish between conduction and transient population anisotropies, polarized time-dependent TRTS and polarized TA scans were compared for (DPC) and (S) samples. Figure 10a shows the photoinduced conductivity and transient absorption decay kinetics of both samples. Parallel and perpendicular excitation data (not shown) were used to calculate “magic angle” excitation traces to represent the pure kinetics of charge carrier motion and population. All time-dependent amplitudes were normalized relative to the largest value of the nonlinear least squares fit of a bi-exponential decay and constant offset model (convoluted with the instrument response), shown as the smooth trace through each dataset. Detailed descriptions of the models and resulting fit parameters applied to both the conduction and transient absorption data are included in the SI see Table S6a.
Figure 10. (a) Normalized 800 nm pump, 1200 nm probe transient absorption (dots/solid lines)contrasted with THz probe transient charge conduction (squares/dashed lines) signals from calculatedmagic angle excitation of PCDTPT samples. The dropcast film (DPC) and dispersion in toluene (S) areindicated by blue and red points/lines, respectively. Lines fit through each represent fitted biexponentialdecay and constant offset models. (b) 2D film (blue) and 3D dispersion (red) anisotropies calculatedusing Equations 1b and 1a, respectively, for the transient absorption (dots/solid lines) and conduction(x’s/dashed lines) signatures shown in (a). The points in (b) (except < 1 ps TA data) are averaged groupsof five time points to improve clarity. Lines represent fitted single exponential decay and constant offsetmodels. The vertical dashed line in each represents the transition from a linear to a logarithmic timescale.

The primary difference between photoinduced conduction (σ) and population (TA) is that chargemotion, σ, decays more rapidly than charge population, TA. Kinetic fits of the TA signal yielded decaylifetimes of 9.1 ps for (DPC) and 4.8 ps for (S), while similar fits of σ yielded decay lifetimes of 2.7 ps for(DPC) and 2.5 ps for (S). Population metrics are sensitive to polaron transient states regardless of theirmobility, while stationary and trapped states do not contribute to conduction signals. Independent ofcharge recombination, where both signals decline, thermal relaxation and localization at trap sites givesrise to charge carriers that contribute to the TA signal but exhibit significantly reduced mobility (and
hence conduction), yielding this observed difference. This localization is more pronounced for the film (DPC, blue) than the solvated polymer (S, red) given the greater difference in the decay lifetimes and longer time delay signal for (DPC). A larger proportion of polarons are locally trapped in the film after several picoseconds than are seen for an electronically isolated PCDTPT sample.

Anisotropies calculated from the TA and $\sigma$ data in Figure 10a are displayed in Figure 10b. Each anisotropy was empirically fit using a single exponential decay and constant offset model (lines), and the corresponding parameters of these fits are included in SI Table S6b. Comparable dipolar anisotropy in both TA populations (solid lines) persists through the 30 ps time window explored here. The $\sigma$ anisotropies (dashed lines) are initially comparable to TA anisotropies and (DPC) tracks reasonably well throughout. Conversely, (S) conduction anisotropy falls off and plateaus at almost half the level of population anisotropy within a few picoseconds of excitation.

Qualitatively, the population anisotropy ($r_{TA}(t)$) is lower for (DPC) than (S) samples with the long delay time constant offset (= thermally relaxed) anisotropies of 0.14 and 0.22 for (DPC) and (S), respectively, though they are closer prior to unequal $\approx 1$ ps decays. The higher anisotropy in (S) TA is elevated in part by the higher theoretical limit for 3D anisotropy (compared to 2D anisotropy for (DPC)); it can also be attributed to the polarons having shorter migration distances prior to entrapment or vibrational relaxation in an uncoupled dispersion compared to a more crystalline film. The anisotropies remaining approximately constant for the remaining duration of the measurement suggests that polaron motion (charge transfer) among the remaining transient population is minimal and perhaps requires substantially more time to yield net motion in a specific direction. The sharpest decline from the initially created anisotropy is seen for (S) conduction, which decreases by 0.19 on the 0.8 ps timescale. Similar to (S) TA data, this provides strong evidence of additional trapping of ordered polarons closer to their generation sites, yielding disproportionally less conduction anisotropy relative to TA anisotropy. Both conduction anisotropies converge to similar 0.14 values, indicating that the mobile carrier population
has comparable polarization memory in (S) and (DPC). However, considering the impact of 3D vs. 2D conduction anisotropy limits suggests that (DPC) anisotropy constitutes less geometric ordering and with less polarization memory in its long-time conduction. The noise floor and limited duration of time delays in the long-time conduction data render exact determination difficult.

CONCLUSIONS

Ultrafast, time-resolved terahertz measurements were conducted to investigate bulk, directional conductivity to enable direct comparison between anisotropically and isotropically prepared polymer films and dispersions. Charge carriers were found to be more mobile along the direction of aligned PCDTPT polymer backbones based on a predisposition for intramolecular coupling, supported by intermolecular ordering, along the propagation length. Comparisons between the charge carrier generation efficiency (or carrier effective mass) depict heavier reliance on the direction of polarized excitation relative to the favored mobility directionality found in each anisotropic polymer film. Carriers were found to scatter more frequently at peak conduction (earliest delay times/upon excitation) and with a greater propensity for charge transfer in films compared to more isolated PCDTPT polymer strands in solvent. This distinction decreases following thermal relaxation with the polymer as a dropcast film and solvated dispersion behaving functionally the same at the longest time-delay (e.g., >1 ps).

It is also noteworthy that conduction signals of similar magnitude were observed for both PCDTPT films and the toluene dispersion. Comparable conduction between polymer dispersions and corresponding films has not been observed by us in other polymers and, to our knowledge, not previously reported in the literature. Comparisons to nominally isotropic P3HT dropcast films and transient absorption measurements revealed differences in the dynamics of the photoinduced charge carrier populations and their conductivities. We believe these differences arise from sensitivity of TA
decays and anisotropies to immobile polarons to which conduction measurements are insensitive.

Ideally, this series of analyses provides the methodology for assessing the local and directional efficacy of comparable materials to facilitate charge transport as components in organic photovoltaic devices and related applications. While these cannot be used to represent pure DC conductive limits, they provide insight into identifying the roots of photoactive charge separation and initial/bulk transport that underlie conductivity in photoactive materials and could be of paramount importance to material/device performance. We plan to extend quantitative studies of related polymeric systems to investigate and contrast their behavior as films and dispersions with this study of PCDTPT samples.

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website at DOI and includes information concerning:

Includes sample preparation details, example polarized UV-vis-NIR and TRTS data, TRTS and TA experimental apparatus and measurement method descriptions, corresponding ungrooved (UG) PCDTPT results including front vs. back surface photoexcitation comparison, frequency-dependent tail dispersion phase comparison, tables of associated parameters and determined quantities listed in the text, and descriptions of error analysis, confidence intervals, and statistical testing methods. (PDF)

AUTHOR INFORMATION

Corresponding Author

* (301) 975-2370, edwin.heilweil@nist.gov

ACKNOWLEDGEMENT
This work was supported by internal NIST (National Institute of Standards and Technology) STRS (Scientific Technical and Research Services). T. J. M. gratefully acknowledges support from the NIST/National Research Council (NRC) postdoctoral associates’ program. S.E. acknowledges support from the U.S. Department of Commerce, NIST under the financial assistance award 70NANB17H305.

ABBREVIATIONS

(DPC), dropcast PCDTPT film; (S), solvated (isolated) PCDTPT in toluene; (G), grooved, bladed PCDTPT film; (UG), ungrooved, bladed PCDTPT film; TA, transient absorption; THz, terahertz; TDS, time domain terahertz spectroscopy; TRTS, time resolved terahertz spectroscopy; FFT, fast Fourier transform; UV-vis-NIR, ultraviolet, visible, near-infrared electronic absorption spectrum; PCDTPT, poly[[1,2,5]thiadiazolo[3,4-c]pyridine-4,7-diyl(4,4-dihexadecyl-4H-cyclopenta[2,1-b:3,4-b’]dithiophene-2,6-diyl)[1,2,5]thiadiazolo[3,4-c]pyridine-7,4-diyl(4,4-dihexadecyl-4H-cyclopenta[2,1-b:3,4-b’]dithiophene-2,6-diyl]; P3HT, poly-3-hexylthiophene; SI, supporting information.

REFERENCES


Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.


Polarization Dependence of Charge Conduction in Conjugated Polymer Films Investigated with Time-Resolved Terahertz Spectroscopy

Supplementary Information:

Timothy J. Magnanelli,¹ Sebastian Engmann,¹,³ Jared K. Wahlstrand,¹ John C. Stephenson,¹ Lee J. Richter,² and Edwin J. Heilweil¹ *

Physical¹ and Material² Measurement Laboratories, National Institute of Standards and Technology (NIST), Gaithersburg, MD, 20899, USA

³Theiss Research, La Jolla, CA, 92036, USA

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1. Acronym List:

- (DPC) = Dropcast PCDTPT film
- (S) = Solvated (isolated) PCDTPT in toluene
- (G) = Grooved, slowly bladed PCDTPT film
- (UG) = Ungrooved, quickly bladed PCDTPT film
- THz = Terahertz
- TDS = Time domain terahertz spectroscopy
- TRTS = Time resolved terahertz spectroscopy
- FFT = Fast Fourier transform
- FWHM = Full width half maximum
- TA = Transient absorption
- UV-vis-NIR = Ultraviolet-visible-near infrared electronic absorption spectrum
- PCDTPT = poly[[1,2,5]thiadiazolo[3,4-c]pyridine-4,7-diyln(4,4-dihexadecyl-4Hcyclopenta[2,1-b:3,4-b']=dithiophene-2,6-diyln)[1,2,5]thiadiazolo[3,4-c]pyridine-7,4-diyln(4,4-dihexadecyl-4H-cyclopenta[2,1-b:3,4-b']=dithiophene-2,6-diyln)
- P3HT = poly-3-hexylthiophene
- CI = Confidence interval

2. Sample Preparation Details

Though the grooves are quite shallow and narrow (~2 nm deep) they rigorously align the bottom of the applied PCDTPT polymer layer and organize additional strands in subsequent layers (two dimensional conductive mats) coaxially along the grooves. This effect gradually tapers off with distance from the substrate. Complementarily, the speed of the film blading procedure influences how the top of the polymer layer aligns as the blade extrudes the polymer across the substrate’s surface. At slow blading speeds (0.1 mm/s to 2 mm/s) the polymer preferentially aligns orthogonal to the blading direction. As this provides the most uniform alignment, it is the preferred rate for aligning the polymer layer to the nanogrooves used in this study. At moderate speeds (2 mm/s to 20 mm/s) the polymer enters what is known as the Landau-Levich regime and aligns along the blading direction while at sufficiently fast blading speeds (> 20 mm/s) the polymer aligns with only slight preference along the blading direction as the process becomes more entropic and less anisotropic. These factors are illustrated by Figure S1 and described at length previously.1
Figure S1. Polymer orientation effects implemented through blading and substrate grooves. Blading aligns polymer strands along the top surface, while grooves (when present) align them near the substrate surface. The grooves are etched perpendicular to the blading direction in this work.

The slow blading speed used for (G)-PCDTPT (0.2 mm/s) aligned this grooved sample in the same direction along its top and bottom surfaces. The rapidly bladed (100 mm/s), ungrooved (UG) sample was nominally intended to be nearly isotropic along the bottom surface and only slightly aligned to the blading direction at the top surface. However, the rapid blading led to discrete, directional sub-domains with a net preferential alignment along the blading direction.

### 3. Polarized UV-vis-NIR Spectra of (G) and (DPC)-PCDTPT Films:

![Polarized UV-vis-NIR Spectra](image)

Figure S2. Polarized UV-vis-NIR spectra collected for the dropcast PCDTPT sample (DPC, blue) and grooved sample (G, red) for orthogonal polarization configurations labeled as 0° and 90° (angles relative to maximum absorption). These examples illustrate preferential steady state absorbance along one polarization axis providing evidence of guided (G) or self- (DPC) organization within the polymer strands. The absorption anisotropy is approximately equivalent across the charge-transfer (centered at 900 nm) and donor π-π* (centered at 450 nm) bands. (G) was collected after data collection (cumulative photodegradation) and prolonged storage (oxidation), which slightly lowered the contrast ratio from that measured during TRTS measurements.
4. Example Time- and Frequency-Domain TDS and TRTS Data and Supplementary Equations:

Figure S3. Prototypical (a) (UG)-PCDTPT TDS time-dependent sweeps with TRTS change in TDS signal following photoexcitation and (b) frequency-dependent FFT of TDS (amplitude of the complex signal). These are presented for a THz probe pulse passing through the sample (E₀) and the measured change in this probe pulse after excitation of the sample (ΔE), scaled by *10 for clarity.

The complex dielectric function (permittivity) is determined by examining the refractive index shift (real part, n₁(ω)) and absorption (imaginary part, n₂(ω)) of the THz waveform through Equations S1a and S1b, respectively. Here, E(ω) and Eᵢ(ω) represent the magnitudes and φ(ω) and φᵢ(ω) the unpacked phases of the photo- or un-excited (φ/E) and through air (φᵢ/Eᵢ) electric fields of the THz probe, respectively. The included constants are c, the speed of light and d, the sample thickness. These refractive index components are used to determine the unexcited, ε₁(ω), and photoexcited, ε̂(ω), dielectric functions using Equations S2a and S2b accordingly. Equation S3 presents the definition of the dielectric functions are complex quantities. These underlying equations facilitate determination of Equation 2 in the main text and are all that are necessary to replicate the results of this work. Additional corrections to the applied pump power: Fresnel losses and absorption affecting ΔN and consideration of sample penetration depth: affecting d, are considered separately.

\[ n_1(\omega) = 1 + \frac{c}{\omega d}(\phi(\omega) - \phi_i(\omega)) \]
\[ n_2(\omega) = -\frac{c}{2\omega d} \ln \left( \frac{|E(\omega)|^2}{|E_i(\omega)|^2} \right) \]  
(S1a, S1b)

\[ \varepsilon_1(\omega) = n_1(\omega)^2 - n_2(\omega)^2 \]
\[ \varepsilon_2(\omega) = 2n_1(\omega)n_2(\omega) \]  
(S2a, S2b)

\[ \hat{\eta}(\omega), \hat{\varepsilon}(\omega) = (\varepsilon_1(\omega) + i \varepsilon_2(\omega)) \]  
(S3)

5. Experimental Laser TRTS and TA Apparatus and Measurement Method:

The Ti³⁺:Sapphire laser system fundamental pulse was generated following regenerative amplification using a Coherent MIRA fs oscillator to seed a Legend amplifier. The amplifier output was a = 1.5 mJ pulse centered at 800 nm with 40 fs FWHM time resolution at a repetition rate of 1 kHz. This pulse was split with a 50:50 beamsplitter and routed down separate lines to generate the photoexcitation pump and THz probe pulses. A small reflection was collected from the pump beam line to serve as the gate pulse for electro-optic sampling (EO) detection. The pump and probe pulses were passed down separate retroreflecting translation stages to control their time delays relative to one another and the gate pulse and through independent laser-
synchronized optical choppers to control iterative phases necessary for spectroscopic analysis. The pump pulse was passed through a half-wave plate to control its polarization. For 400 nm studies, a Type I beta-barium borate (BBO) crystal was inserted in the 800 nm pump beam to produce 400 nm light through second harmonic generation (SHG). The excitation power was attenuated to ≈ 20 µJ to 40 µJ to avoid sample degradation. These powers were previously found to be within a linear regime for absorption and photoconductive response for studies of P3HT (400 nm) and confirmed here (for 800 nm).5

The THz probe pulse was produced by a 2 mm thick ZnTe <110> crystal to generate radiation from 0.25 THz to 2.75 THz. Residual 800 nm was filtered out using a low-density foam filter and the cross-correlation time resolution of the excitation and probe pulse generated in this manner was ≈ 200 fs. The THz probe beam was collimated and focused onto the sample by two off-axis parabolic mirrors, the second of which has a hole drilled through its surface (just off-centered) to allow for the pump beam to overlap at the sample. The ZnTe crystal was rotated to generate the THz probe with vertical polarization (relative to the laser table), and the polarization was further cleaned up after the sample using a metal wire-grid polarizer set to match the blading direction and pump polarizations in an all parallel configuration. The probe beam was collimated and re-focused by parabolic mirrors through a thin gallium arsenide (GaAs) wafer and then into a second ZnTe detection crystal for electro-optic (EO) detection. The weak gate pulse was passed off the front surface of the GaAs beam combiner and routed collinearly to the detection crystal. The gate pulse was then passed through a quarter waveplate and Wollaston polarizing beam splitter, from which each polarization was routed to two matched Si PIN photodiodes. The voltages from these were filtered and amplified as a difference signal on a Stanford 830 lock-in amplifier4 at the repetition rate of the applicable chopper for the measurement; the pump line chopper was used to collect pump-induced t- or v-dependent and probe line chopper for v-dependent ground state spectra. Spectra were collected as time-dependent traces through readout of the analog voltage output of the “A-B” signal of the lock-in amplifier and processed using LabVIEW to average multiple sweeps and exported for analysis. Voltage outputs were split to a second lock-in amplifier ((DPC) and (S)) to allow ΔE and E0 to be measured simultaneously by using the same “A-B” signal and locking onto each (unequal) frequency of an optical chopper.

Transient absorption (TA) measurements were conducted using a 1 MHz, 40 W, and 1028 nm fundamental femtosecond laser (Light Conversion Carbide 40).4 A fraction of the fundamental pumped an optical parametric amplifier (OPA) to generate 800 nm, 150 fs FWHM excitation pulses. Another small portion of the fundamental laser output was used to generate a broadband supercontinuum (SC). Second-order chirp of the SC was compensated using a grating compressor. The repetition rate was reduced to 100 kHz to mitigate laser-induced sample degradation. The pump-probe delay time was controlled using an optical delay stage. The FWHM spot sizes of the pump and probe were ≈ 200 µm and 100 µm, respectively. The transmitted probe beam was filtered to 1200 +/- 10 nm by a single grating monochromator and detected by an InGaAs diode at the exit slit. The pump-induced change in the probe beam near 1200 nm was detected using a lock-in amplifier referenced to an optical chopper in the pump beam. When measuring TA of the (DPC) film, the birefringent nature of the polymer layer was found to scramble the polarization ratio of the transmitted probe from an extinction ratio of > 70:1 to 12:1. To determine the time resolution for the TA experiment, the cross correlation between the 1200 nm SC and 800 nm pump was measured by frequency summing in a 10 µm long BBO crystal placed at the PCDTPT sample position. The 480 nm sum
frequency signal was routed to the same spectrometer used for the TA measurements, and the cross correlation was found to have a FWHM of 0.25 ps.

6. (UG)-PCDTPT Film Analysis and Comparison to (G)-PCDTPT:

![Graphs and images related to the analysis of (UG)-PCDTPT film](image-url)

**Figure S4.** Corresponding results for the (UG)-PCDTPT film using the same analyses for sample (G) in the main text. (a) Time-dependent TRTS sweeps (analogous to Figure 4a for (G)), (b) two-dimensional conduction anisotropy for peak and tail conduction (Figure 5), (c) frequency-dependent peak conduction (Figure 6a), and (d) extracted mobility (blue) and charge yield (yellow) for the peak conduction under different polarization configurations (Figure 7a).

The equivalent analysis of (UG) data (to (G)) was excluded from the main manuscript as it largely mirrored the trends shown for (G), though with more favorable conduction in the blading direction rather than orthogonally to it. Except for (UG) excited at 800 nm, each sample was excited through the back of the substrate, with the pump incident to the bottom surface of the polymer layer. In contrast to the (G) sample anisotropies, (UG) excited at 800 nm displays a positive anisotropy for excitation parallel to the blading direction and negative anisotropy for perpendicular excitation and preferential conduction along the blading direction regardless of excitation orientation. As was found similarly with (G), charges are found to be more mobile for (UG) along the polymer propagation direction facilitating conduction and yielding conduction anisotropy.
7. Front vs. Back (UG)-PCDTPT Excitation Comparison:

Figure S5. Peak and tail conduction anisotropies calculated for 800 nm excitation of ungrooved (UG)-PCDTPT excited through the front and back substrate surfaces for each polarization configuration (comparable to Figure 6 in the main text). Parallel and perpendicular directions represent pump:blade polarization alignment. (UG)-PCDTPT primarily exhibits more positive anisotropic behavior when excited from the back, counter to expectations.

This analysis corroborates the steady state findings that the top exposed polymer layer is predominantly aligned along the blading direction.1 This also explains the observation of conduction anisotropy relying more on sample orientation when excited through the top film surface producing dominant conduction along the pump dipole direction (i.e. more positive anisotropies) than when excited through the back of the substrate. Interestingly, the anisotropies of front and back excitation are nearly equivalent at the peak but deviate at long time delays. This comparison reveals a discrepancy between excitation of primarily the front side (film outer surface, aligned to the blading direction) and the back side (bottom at substrate interface, more randomly aligned) on the resulting conduction anisotropies. These experiments revealed strong agreement with the front side 800 nm results presented in Figure S4b (i.e., the (UG) sample was mistakenly analyzed using front side excitation for that data set). These optically anisotropic, interfacial-dependent results qualitatively mimic X-ray diffraction results (not included) seen previously for similarly prepared films,1 though X-ray analysis of (UG) revealed the prevalence of non-uniformly aligned sub-domains.
8. Mobility ($\mu_T$) and Charge Generation Efficiency ($\Phi_{eff}$) from (S) and (DPC)-PCDTPT Tail Data:

![Figure S6](image)

**Figure S6.** Mobility values ($\mu_T$, blue and $\mu_{TDS}$, gray) and charge yield efficiency ($\Phi_{eff}$, brown) calculated for averaged tail (long time) data of PCDTPT dispersion (S) and dropcast film (DPC). Error bars for 95% confidence intervals are too large to be displayed. $\mu_{TDS}$ values have been multiplied by a factor of 4 to permit comparison.

Here, we explore a more in-depth breakdown of long-time delay (thermally relaxed) mobility ($\mu_T$ and $\mu_{TDS}$) and charge yield ($\Phi_{eff}$) (as in Figure 7) derived from $v$-dependent traces (similar to Figure 8) of data shown in Figure 10b. This comparison highlights that the major discrepancy between measured conduction anisotropy (TRTS) of (DPC) and (S) at the thermalized limit arises from a difference in relative mobility (blue) between each polarization configuration, not the charge yield/effective mass (brown). Estimated errors associated with these values suggest the results are not statistically significant. However, self-consistency within the datasets suggests that the cause of deviation in long-time conduction anisotropy between (S) and (DPC) is related to elevated orthogonal mobility in orthogonal carriers of (S). In $\mu_T$, perpendicular (S) counteracts some of the anisotropy established by $\Phi_{eff}$ effects, though this becomes negligible when considering $\mu_{TDS}$, where all values are reasonably close.

9. Tables of (G), (UG), (DPC), and (S)-PCDTPT and P3HT Properties and Fit Parameters:

**Table S1:** Specific characteristics of PCDTPT samples. Absorption ($\alpha$) values varied between measurements due to sample heterogeneity, and slight degradation with time. The penetration depth used for calculations is assumed to be the shorter of $2/\alpha$ (the 1/e absorption coefficient) and the sample thickness.

| Sample | 800 nm $\alpha$ || / ⊥ | Penetration depth (nm) | Thickness (nm) |
|--------|-----------------|-----------------|----------------------|-----------------|
| (G)    | 0.35 / 0.88     | 394 / 158       | 320                  |
| (UG)   | 1.10 / 0.67     | 95 / 156        | 240                  |
| (DPC)  | 0.93 / 1.22     | 116 / 90        | 250                  |
| (S)    | 0.99            | ---             | 1.00 (mm)            |
**Table S2a:** Peak conduction anisotropies determined for (G) and (UG)-PCDTPT and P3HT under different pump frequencies and polarization orientations (relative to the anisotropic material layering) corresponding to Figures 5 and S4b. Errors are given as the linearized 95% confidence intervals (CI) or +/- two standard deviations.

| Sample | 800 || | 800 | 400 || | 400 |
|--------|------|------|------|------|------|------|------|
| (G)    | -0.073 ± 0.108 | 0.576 ± 0.170 | -0.214 ± 0.100 | 0.406 ± 0.081 |
| (UG)   | 0.471 ± 0.101 | -0.087 ± 0.082 | 0.318 ± 0.115 | -0.574 ± 0.116 |
| P3HT   | --- | --- | 0.100 ± 0.009 | --- |
| 800 nm | 800 nm | Front || | Front | Back || | Back |
| (G)    | 0.413 ± 0.080 | 0.469 ± 0.082 | 0.025 ± 0.073 | -0.002 ± 0.079 |

**Table S2b:** Tail (e.g., averaged long delay times) conduction anisotropies determined for (G) and (UG)-PCDTPT, and P3HT samples under different pump frequencies and polarization orientations (relative to the anisotropic material layering). These values correspond to Figures 5 and S4.

| Sample | 800 || | 800 | 400 || | 400 |
|--------|------|------|------|------|------|------|------|
| (G)    | -0.285 ± 0.170 | 0.684 ± 0.170 | -0.112 ± 0.111 | 0.625 ± 0.296 |
| (UG)   | 0.280 ± 0.151 | -0.304 ± 0.114 | 0.684 ± 0.151 | -0.387 ± 0.101 |
| P3HT   | --- | --- | 0.175 ± 0.028 | --- |
| 800 nm | 800 nm | Front || | Front | Back || | Back |
| (UG)   | 0.330 ± 0.098 | 0.472 ± 0.095 | -0.228 ± 0.106 | 0.098 ± 0.075 |
Table S3: Frequency dependent parameters for PCDTPT and P3HT peak fits collected for 800 nm (400 nm, P3HT) photoexcitation. Polarizations are indicated as pump:blade (PuB) and probe:blade (PrB) for (G) and (UG) and pump:probe (PP) for others. Relative ΔNq2/m*’s are corrected for excitation fluence, not absorptivity or penetration depth. Uncertainties are shown as nonlinear least squares regression 95 % CIs.

<table>
<thead>
<tr>
<th>(G) PuB / PrB</th>
<th>(Relative) ΔNq²/m* (95% CI)</th>
<th>τ (fs) (95% CI)</th>
<th>c₁ (95% CI)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>/</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>/ ⊥</td>
<td>3.85 (2.88 – 5.46)</td>
</tr>
<tr>
<td>⊥ / ⊥</td>
<td>8.07 (5.60 – 11.28)</td>
<td>66 (50 – 82)</td>
<td>-0.702 (-0.765 – -0.638)</td>
</tr>
<tr>
<td>⊥ /</td>
<td></td>
<td></td>
<td>3.22 (2.19 – 5.34)</td>
</tr>
<tr>
<td>(UG) PuB / PrB</td>
<td>(Relative) ΔNq²/m* (95% CI)</td>
<td>τ (fs) (95% CI)</td>
<td>c₁ (95% CI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>/</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>/ ⊥</td>
<td>4.75 (3.47 – 7.51)</td>
</tr>
<tr>
<td>⊥ / ⊥</td>
<td>4.83 (3.19 – 7.00)</td>
<td>63 (44 – 78)</td>
<td>-0.805 (-0.882 – -0.731)</td>
</tr>
<tr>
<td>⊥ /</td>
<td></td>
<td></td>
<td>4.81 (3.51 – 6.55)</td>
</tr>
<tr>
<td>(DPC) PP</td>
<td>(Relative) ΔNq²/m* (95% CI)</td>
<td>τ (fs) (95% CI)</td>
<td>c₁ (95% CI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.64 (5.16 – 14.3)</td>
</tr>
<tr>
<td>⊥</td>
<td>7.92 (4.70 – 23.3)</td>
<td>24 (12 – 35)</td>
<td>-0.741 (-0.807 – -0.706)</td>
</tr>
<tr>
<td>(S) PP</td>
<td>(Relative) ΔNq²/m* (95% CI)</td>
<td>τ (fs) (95% CI)</td>
<td>c₁ (95% CI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.39 (1.95 – 2.98)</td>
</tr>
<tr>
<td>⊥</td>
<td>1.32 (0.92 – 2.09)</td>
<td>52 (14 – 69)</td>
<td>-0.958 (-1 – -0.911)</td>
</tr>
<tr>
<td>P3HT PP</td>
<td>(Relative) ΔNq²/m* (95% CI)</td>
<td>τ (fs) (95% CI)</td>
<td>c₁ (95% CI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.50 (1.67 – 4.03)</td>
</tr>
<tr>
<td>⊥</td>
<td>3.83 (1.92 – Unbounded)</td>
<td>38 (14 – 69)</td>
<td>-0.671 (-0.749 – -0.570)</td>
</tr>
</tbody>
</table>
Table S4: Peak mobility with ($\mu_P$) and without ($\mu_{PDS}$) incorporation of the Drude Smith backscattering parameter ($c_1, \text{cm}^2/\text{Vs}$) and charge yield efficiencies (%$\Phi_{eff} * 100$) of (G), (UG), (DPC), and (S)-PCDTPT and P3HT. Polarization configurations are indicated by pump:blade / probe:blade ((G) and (UG)) or pump:probe (PP, (DPC) and (S)). These values were determined from analyzing $\nu$-dependent data shown in Figures 6, S4c, 8, and additional unshown data. Each range in parenthesis represents the parameter’s 95% confidence interval. CIs for $\mu_{PDS}$ are proportionally $\approx$ to those for $\mu_P$ following propagation and are omitted for brevity.

<table>
<thead>
<tr>
<th>PuB / PrB</th>
<th>(G) $\mu_P$ / $\mu_{PDS}$</th>
<th>(G) %$\Phi_{eff} * 100$</th>
<th>(UG) $\mu_P$ / $\mu_{PDS}$</th>
<th>(UG) %$\Phi_{eff} * 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td></td>
<td>/</td>
<td></td>
<td>$</td>
</tr>
<tr>
<td></td>
<td>(531 – 1288)</td>
<td>(2.27 – 5.49)</td>
<td>(1073 – 1670)</td>
<td>(1.69 – 2.98)</td>
</tr>
<tr>
<td>$</td>
<td></td>
<td>/\perp$</td>
<td>1182 / 383</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>(834 – 1578)</td>
<td>(1.96 – 3.72)</td>
<td>(834 – 1516)</td>
<td>(0.81 – 1.75)</td>
</tr>
<tr>
<td>$\perp/\perp$</td>
<td>1310 / 390</td>
<td>3.16</td>
<td>1250 / 244</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>(937 – 1889)</td>
<td>(2.19 – 4.42)</td>
<td>(873 – 1546)</td>
<td>(1.29 – 2.83)</td>
</tr>
<tr>
<td>$\perp/</td>
<td></td>
<td>$</td>
<td>1033 / 292</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>(623 – 1519)</td>
<td>(0.86 – 2.1)</td>
<td>(996 – 1608)</td>
<td>(1.26 – 2.36)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PP</th>
<th>(DPC) $\mu_P$ / $\mu_{PDS}$</th>
<th>(DPC) %$\Phi_{eff} * 100$</th>
<th>(S) $\mu_P$ / $\mu_{PDS}$</th>
<th>(S) %$\Phi_{eff} * 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td></td>
<td>$</td>
<td>517 / 133</td>
<td>3.97</td>
</tr>
<tr>
<td></td>
<td>(336 – 685)</td>
<td>(2.68 – 7.46)</td>
<td>(982 – 1273)</td>
<td>(1.76 – 2.67)</td>
</tr>
<tr>
<td>$\perp$</td>
<td>474 / 123</td>
<td>3.00</td>
<td>1026 / 43</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>(231 – 688)</td>
<td>(1.78 – 8.81)</td>
<td>(777 – 1274)</td>
<td>(0.83 – 1.88)</td>
</tr>
<tr>
<td>P3HT</td>
<td>$\mu_P$ / $\mu_{PDS}$</td>
<td>%$\Phi_{eff} * 100$</td>
<td>$\mu_P$ / $\mu_{PDS}$</td>
<td>%$\Phi_{eff} * 100$</td>
</tr>
<tr>
<td>$</td>
<td></td>
<td>$</td>
<td>612 / 84</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>(431 – 814)</td>
<td>(6.5 – 15.7)</td>
<td>(121 – 577)</td>
<td>(7.4 – unbounded)</td>
</tr>
</tbody>
</table>

Specific values used for Figures 7 (main text) and S4d are shown here to allow quantitative comparison. Equations 4a and S4 are separate but similar ways to estimate mobility from the fitted scattering time ($\tau$) and the comparing $\Delta N$ to the original $\Delta \sigma$ data, respectively. Since the latter equation involves fitting the original conductivity data with a known $\Delta N$, it still accesses the same information encoded by $\tau$. Both are heavily dependent on the value selected for $m^*$ and give qualitatively similar results (+/− 25%).

$$\mu = \frac{\Delta \sigma}{e\Delta N}$$  \hspace{1cm} (S4)

While the resulting anisotropies would be different for the results using Equation 4a or S4, we opted for the former given the precedent set by previous work\(^6\) and lack of clear rationale for selecting either method in particular. The errors associated with Equation S4 were reasonably higher than those from Equation 4a from the inclusion of additional parameters in the final mobility determination. Mobility determined for each sample from Equation S4 is included in Table S5 below while Equation 4a was used to calculate the results in Table S4.
Table S5: Mobility (cm$^2$/Vs) for (G) and (UG)-PCDTPT determined using Equation S4 for the associated polarization configurations expressed as pump:blade / probe:blade (pump:probe).

<table>
<thead>
<tr>
<th>PuB / PrB (PP)</th>
<th>(G) $\mu_P$ (95% CI)</th>
<th>(UG) $\mu_P$ (95% CI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td></td>
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<tr>
<td>$</td>
<td></td>
<td>/ \perp$</td>
</tr>
<tr>
<td>$\perp /</td>
<td></td>
<td>$</td>
</tr>
<tr>
<td>$\perp / \perp$</td>
<td>1078 \hspace{1em} (651 – 1585)</td>
<td>1671 \hspace{1em} (1227 – 2292)</td>
</tr>
</tbody>
</table>

Table S6a: Fit parameters (and 95% CIs) for empirical TA and conduction ($\sigma$) models shown in Figure 10a.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(S) TA(t)</th>
<th>(DPC) TA(t)</th>
<th>(S) $\sigma$(t)</th>
<th>(DPC) $\sigma$(t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRF$_0$ (Offset)</td>
<td>-0.103</td>
<td>-0.082</td>
<td>0.260</td>
<td>0.140</td>
</tr>
<tr>
<td>IRF$_w$ (Width)</td>
<td>0.154 \hspace{1em} (0.136 – 0.173)</td>
<td>0.179 \hspace{1em} (0.163 – 0.196)</td>
<td>0.301 \hspace{1em} (0.284 – 0.319)</td>
<td>0.263 \hspace{1em} (0.253 – 0.273)</td>
</tr>
<tr>
<td>$A_1$</td>
<td>0.527 \hspace{1em} (0.484 – 0.574)</td>
<td>0.496 \hspace{1em} (0.454 – 0.543)</td>
<td>1.502 \hspace{1em} (1.349 – 1.771)</td>
<td>1.678 \hspace{1em} (1.558 – 1.867)</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>0.619 \hspace{1em} (0.507 – 0.745)</td>
<td>0.701 \hspace{1em} (0.590 – 0.825)</td>
<td>0.274 \hspace{1em} (0.212 – 0.328)</td>
<td>0.251 \hspace{1em} (0.210 – 0.284)</td>
</tr>
<tr>
<td>$A_2$</td>
<td>0.271 \hspace{1em} (0.239 – 0.303)</td>
<td>0.380 \hspace{1em} (0.364 – 0.395)</td>
<td>0.164 \hspace{1em} (0.123 – 0.228)</td>
<td>0.170 \hspace{1em} (0.140 – 0.216)</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>4.78 \hspace{1em} (4.22 – 5.51)</td>
<td>9.05 \hspace{1em} (8.20 – 10.13)</td>
<td>2.51 \hspace{1em} (1.74 – 3.83)</td>
<td>2.66 \hspace{1em} (2.00 – 3.50)</td>
</tr>
<tr>
<td>$A_3$</td>
<td>0.068 \hspace{1em} (0.064 – 0.072)</td>
<td>0.085 \hspace{1em} (0.075 – 0.094)</td>
<td>0.052 \hspace{1em} (0.046 – 0.057)</td>
<td>0.038 \hspace{1em} (0.035 – 0.041)</td>
</tr>
</tbody>
</table>

Table S6b: Fit parameters for the transient absorption and conduction anisotropies shown in Figure 10b.

<table>
<thead>
<tr>
<th>$r(t)$</th>
<th>(S) $r_{TA(t)}$</th>
<th>(DPC) $r_{TA(t)}$</th>
<th>(S) $r_{\sigma(t)}$</th>
<th>(DPC) $r_{\sigma(t)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>0.109 \hspace{1em} (---)</td>
<td>0.133 \hspace{1em} (0.066 – 2.941)</td>
<td>0.066 \hspace{1em} (0.022 – 0.273)</td>
<td>0.192 \hspace{1em} (0.066 – 3.26)</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>0.230 \hspace{1em} (---)</td>
<td>0.737 \hspace{1em} (0.256 – 1.636)</td>
<td>10.14 \hspace{1em} (0.30 – 223)</td>
<td>0.761 \hspace{1em} (0.063 – 1.50)</td>
</tr>
<tr>
<td>$B_2$</td>
<td>0.223 \hspace{1em} (0.213 – 0.233)</td>
<td>0.144 \hspace{1em} (0.136 – 0.150)</td>
<td>0.139 \hspace{1em} (0 – 0.197)</td>
<td>0.138 \hspace{1em} (0.097 – 0.169)</td>
</tr>
</tbody>
</table>
The empirical fits used for the data shown in Figures 10a and 10b are described in Equations S5a and S5b with optimized parameters included in Tables 6a and 6b, respectively. Equation S5a represents a Gaussian instrument response function (IRF) convoluted with a bi-exponential decay and constant offset model to determine TA(t) and σ(t) extracted by determining the “magic angle”, isotropic representation from each pair of parallel and perpendicular data (not shown). Here, * signifies a convolution of the two functions. For Figure 10b, a single exponential decay and constant offset model to fit rTA(t) and rσ(t) (Equation S5b) beginning at the peak anisotropy (~25% rise of the signal). The instrument response is insignificant practically for fitting anisotropy data, as these trends should principally plateau to a finite maximum at early time delays owing to the instantaneous generation of polarized transient states.

\[
TA(t), \sigma(t) = e^{-\frac{4\ln(2)(t-\text{IRF}_D)^2}{\text{IRF}_w^2}} \ast \left( A_1 e^{-(\frac{t}{\tau_1})} + A_2 e^{-(\frac{t}{\tau_2})} + A_3 \right) \quad (\text{S5a})
\]

\[
r_{TA}(t), r_{\sigma}(t) = B_1 e^{-(\frac{t}{\tau_1})} + B_2 \quad (\text{S5b})
\]

10. Error Analysis, Confidence Intervals, and Statistical Testing:

Uncertainties throughout the manuscript were determined depending on the specific application. When applicable, i.e. considering linear samples or iterations of repeated experiments, values were numerically averaged with standard deviations of those averages used to represent the error along with ordinary uncertainty propagation in quadrature. For nonlinear least square regression parameters and results, i.e., to estimate ΔN, τ, c1, σDC, and others, the procedure described in detail below was used to obtain the associated nonlinear 95% confidence intervals. Errors were assumed linearizable to the extent of ordinary propagation in quadrature for determining the uncertainties of quantities calculated from these extracted parameters (i.e. μ and Φeff).

For a given nonlinear least squares regression model, containing n data points and k adjustable parameters, the model was initially optimized using a Marquadt-Levenberg optimization algorithm (starting at a reasonable initial guess) to determine an optimal fit. The values for each of the parameters were reported as these optimized values. To determine the uncertainty associated with a single adjustable parameter, x, an F-test was performed using the following procedure7:

1. Perturbing the parameter, x, of interest by fixed increments and re-optimizing the remaining k-1 parameters at each unique value of x.
2. Calculating the X² (chi-squared) of each fit relative to the X² of the optimal fit.
3. Assessing the range of relative X² values to determine the point at which they exceed a critical value defined by looking up F(k, n-k) at 95% confidence from an F-distribution table.
4. Individual parameters from the same model were repeated by fixing only the parameter of interest and allowing the rest to converge to new values for re-optimized fits.

This procedure results in nonlinear 95% CIs, with unequal positive and negative error bounds. This methodology requires some degree of local linearity, continuity, and unique convergence to parameters of the associated model but is sufficient for the simple models described in this work.

Though the differences between values given in the tables and in figures from the main text appear close due to large error bounds (+/- 95%) many discussed in the paper exhibit statistically significant differences. In particular, the difference between each pair of mobility values for (G) is statistically
significant when employing a two-sample t-test analysis. This assumes normalized distributions for error uncertainties (i.e. standard deviations) and that each frequency can be used to predict a mobility through the model (nonlinear least squares regression) to provide an appropriate “statistical” sample. Given the potential for over-resolved data from limited temporal resolution and padding of times prior to applying the Fourier Transform, the “sample size”, related to the degrees of freedom the nonlinear regression, was precautionarily divided by two. Under these circumstances, and if and only if the associated p-value is less than 0.025 for a two-sided test at 95% confidence, we conclude that the differences are statistically significant as typified by Table S7 below.

Table S7: Statistical testing between the (G) peak mobilities predicted for || / || vs. || / || and || / || vs. || / || with polarization configurations given as pump:blade / probe:blade (Pu:B/Pr:B).

<table>
<thead>
<tr>
<th>(G) Pu:B/Pr:B</th>
<th>µPeak</th>
<th>St. Dev.</th>
<th>n</th>
<th>t-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>/</td>
<td></td>
<td></td>
<td>1182</td>
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<td>903</td>
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<td>1033</td>
</tr>
</tbody>
</table>

These examples do not indicate that every pair of values are significantly different, simply that the differences can be more significant than they would appear given the size of the associated error bars. Thus, we are confident in deriving qualitative conclusions about why certain anisotropies, mobilities, and charge conduction yields are significantly different despite overlapping 95% CIs.

11. Supporting Information References:


(2) Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

