Anisotropic Charge Conduction in Oriented Donor-Acceptor Polymer Films and Liquid Dispersions Measured by Time-Resolved Terahertz Spectroscopy

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***Abstract*—Time-Resolved Terahertz methods with polarized pump-probe analysis are employed to extract conduction and mobility anisotropy of conjugated donor-acceptor polymers as films and liquid dispersions. Nano-grooved substrates with bladed films yield high in-chain conduction anisotropy compared to near isotropic drop-cast films and polymers in toluene.**

I. INTRODUCTION

POLARIZATION anisotropy measurements of charge conduction in oriented films, isotropic films and liquid dispersions of the block co-polymer PCDTPT, consisting of alternating cyclopenta-dithiophene (D-donor) and thiadiazolo-pyridine (A-acceptor) units and related D-A species are presented.[1] While Terahertz (THz) conduction in polymeric films is typically evaluated using unspecified polarizations, measurement with specifically oriented pump-probe polarized fields enables extraction of sample-dependent anisotropic conduction. Comparisons are made among PCDTPT films and dispersions and to the traditional photoconductive polymer poly-3-hexylthiophene (P3HT). We also report population anisotropy for aligned PCDTPT samples using transient polarized electronic absorption spectroscopy.

In this work, conduction anisotropy is directly measured using linearly polarized femtosecond excitation pulses (400 nm and 800 nm) and polarized THz probe pulses. Film preparation techniques that affect sample morphology, including substrate nanoscale etched grooves and blading speed, facilitate polymer alignment and are compared to more randomized films and liquid toluene dispersions. Room temperature Time-Domain Terahertz (TDS) and Time-Resolved Terahertz (TRTS) spectroscopic measurements with Drude-Smith analysis yields the excitation-probe polarization conductivity dependence, extracted carrier mobility, scattering times and generation efficiencies.

We also report that related donor-acceptor polymers in more isotropic environments (e.g., dropcast films and toluene dispersions) yield conduction signals comparable to ordered films. This is not the case for P3HT and the same D-A polymers solubilized in chlorinated solvents. Time permitting, these findings and qualitative interpretations of polymer structure-conduction relationships will be discussed.

II. RESULTS

Comparisons are first made among PCDTPT films of different ordering and to the traditional photoconductive polymer poly-3-hexylthiophene (P3HT, Fig. 1). We will also compare the anisotropic conduction response of grooved PCDTPT films (G), un-grooved (UG) films and toluene dispersions to the polarized electronic (population) response using transient absorption with 1200 nm probe pulses.

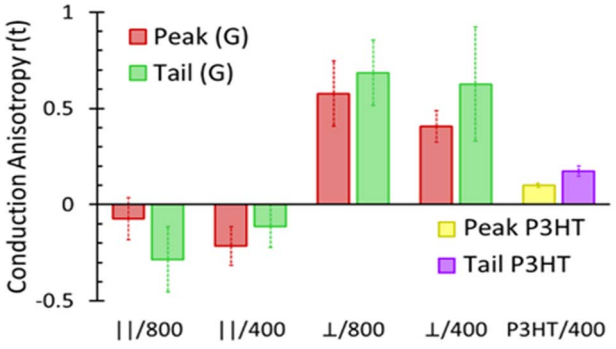

Fig. 1. Conduction anisotropy for (G)-PCDTPT and P3HT films extracted from the photoexcited peak (red/yellow bars) and delayed tail (green/purple bars) for TRTS conduction signals. The bottom axis labels indicate the excitation polarization orientation to the blading direction (pump:blade) and excitation wavelength (nm). Error bars represent 95 % confidence intervals.

As an example, the frequency-dependent conductivity for the PCDTPT toluene dispersion (S) is shown in Fig. 2 and similar signal magnitudes are found for the (G) film. We find the real DC conductivity approaches zero while the scattering time (τ) decreases. Results for other D-A polymers are similar.

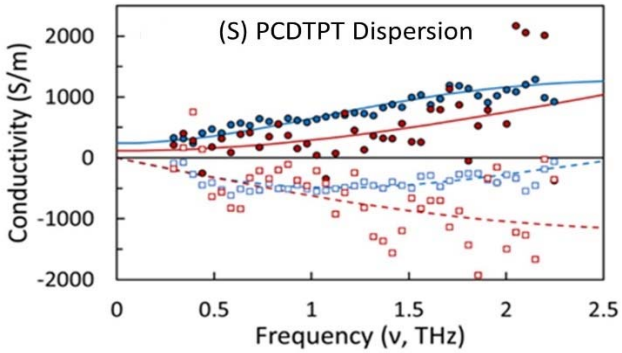

Fig. 2. Real (circles/solid fit) and imaginary (squares/dashed fit) conductivity for peak (blue) and 20 ps delayed tail (red) for a PCDTPT toluene dispersion (S) with 800 nm excitation fluence 0.98 mJ/cm^2. Tail conductivity multiplied by 15. (S) conductivity is calculated using a film equivalent thickness for the absorption observed through a 1 mm pathlength liquid cell.

III. SUMMARY

Polarization charge anisotropy originates from conduction along PCDTPT chains. Dispersions exhibit strong localized THz conductivity suggesting similar photon-to-charge conversion and thermally relaxed dynamics as in films.

REFERENCES

[1]. T.J. Magnanelli, S. Engmann, J. K. Wahlstrand, J. C. Stephenson, L. J. Richter and E. J. Heilweil, "Polarization Dependence of Charge Conduction in Conjugated Polymer Films Investigated with Time-Resolved Terahertz Spectroscopy," *J. Phys. Chem. C*, accepted March 6, 2020. See: https://dx.doi.org/10.1021/acs.jpcc.9b11870