

Optically-Tunable Organic Semiconductor Heterojunction P3HT-PCBM for Millimeter-wave Applications

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Abstract—The dielectric constant of a photo-sensitive organic semiconductor heterojunction poly(3-hexylthiophene) (P3HT, 95%) and [6,6]-Phenyl C61 butyric acid methyl ester (PCBM, 5%) is estimated using its transmission response using a vector network analyzer driving a quasi-optical (QO) transmissometer. White-light irradiance of 65mW/cm² over an area of 2.27cm² is used to promote the photo-induced dielectric response of the organic polymer blend; so defining the ‘active’ state. Estimation of the complex permittivity of the polymer-blend is undertaken for both inactive (dark-state), and active state conditions to observe its tunable dielectric range over the WR-3 waveguide band (220-325 GHz).

I. INTRODUCTION

IN recent years, organic semiconductors have been recognized as useful tunable materials for applications in both polymer electronics and optically controlled microwave devices [1, 2]. In opto-electronic devices, organic polymers serve as fundamental elements due to their functionality, cost-effectiveness, and capability of thin-film, large-area and flexible device fabrication [3]. Use of organic polymers as tunable materials in phase-shifting devices has also been reported in literature [2]. Tang et.al reported a 10% change in permittivity of the organic polymer P3HT when optically-activated leading a phase shift of 10° between the input and output ports of a transmission line. Verification of such a statement requires measurement of the permittivity of the polymer in both on and off states over a wide frequency domain to analyze the possible phase-shifting applications of such a polymer-blend.

Regioregular poly(3-hexylthiophene) (RR P3HT) is an ideal conjugated polymer for polymer-based photovoltaic (PV) cells. It has been reported that photo-induced carriers in P3HT tend to have a higher mobility compared to most commercial organic semiconductors, because it forms a semi-crystalline, lamellar structure during spin-casting [4]. Additionally, P3HT has a bandgap of 1.9 eV, suitable for photo-excitation of free carriers from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). The high drift mobility of P3HT induced charge carriers and its optical absorption properties make this organic semiconductor an appropriate choice for use in photo-controlled phase-shifters [5]. P3HT is applied here by spray-coating onto any hard surface when dissolved with organic solvents. Popular methods of deposition onto substrates are by drop casting and spin coating.

The blend, ratio of 95% P3HT: 5% PCBM was chosen over neat P3HT because in organic polymers very few excited states tend to undergo dissociation [6]. By adding a different band gap polymer (here, PCBM), to base polymer (P3HT), the organic nature of P3HT is distorted and the dissociation of free electrons is promoted. Consequently, the number of photo-

generated carriers in the active region of the polymer-blend, or heterojunction, is expected to be more in number than for pure P3HT.

II. RESULTS

The sample blend of 95% P3HT: 5% PCBM was prepared with 2.4 mg of PCBM and 48.6 mg of P3HT along with 1.5 ml of the low boiling point organic solvent chloroform to dissolve the organic polymer blend. A thin mylar film was glued over a circular hole drilled through a rectangular, metal, sample-holder. The fluid sample blend was then drop-cast from the reverse side onto the mylar film (see Fig. 1 a). The sample holder was placed on a hot plate at 60°C in order for the sample to be evenly deposited.

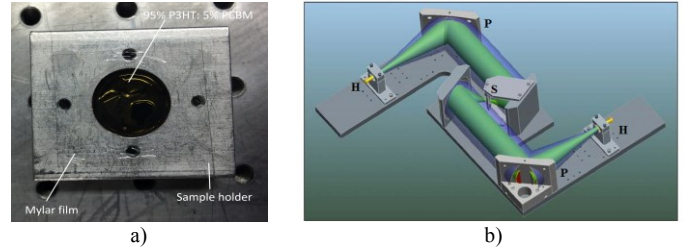


Fig. 1 a) Front view of the rectangular metallic sample holder (S) with sample (95% P3HT:5% PCBM) drop-casted onto a thin supporting Mylar film through the central cylindrical cut-out of the holder b) Schematic of a quasi-optic millimeter-wave transmission measurement setup (H: feeding horns; P: parabolic mirrors; S: Sample holder)

Measuring calibrated complex transmission data, and knowing the thickness of sample, d_s , and mylar d_m , ABCD matrix theory is used to estimate the real and imaginary part of the complex permittivity of the organic blend [7].

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} = \begin{bmatrix} \cos\left(\frac{\omega d_s \sqrt{\epsilon_r}}{c}\right) & jZ \sin\left(\frac{\omega d_s \sqrt{\epsilon_r}}{c}\right) \\ j/Z \sin\left(\frac{\omega d_s \sqrt{\epsilon_r}}{c}\right) & \cos\left(\frac{\omega d_s \sqrt{\epsilon_r}}{c}\right) \end{bmatrix} \quad (1)$$

Z is the wave impedance of the material, ω is the angular frequency and c has its usual meaning of the speed of light in free-space. The ABCD transfer matrix can be used to estimate the transmittance of the material under test using the following equation.

$$T = \frac{2Z_0}{AZ_0 + B + CZ_0^2 + DZ_0} \quad (2)$$

where, Z_0 is the wave impedance of free space. For a multilayered structure, the transfer matrix is expressed as

$$T_{total} = \begin{bmatrix} A_{total} & B_{total} \\ C_{total} & D_{total} \end{bmatrix} = \begin{bmatrix} A_1 & B_1 \\ C_1 & D_1 \end{bmatrix} \begin{bmatrix} A_2 & B_2 \\ C_2 & D_2 \end{bmatrix} \dots \dots \quad (3)$$

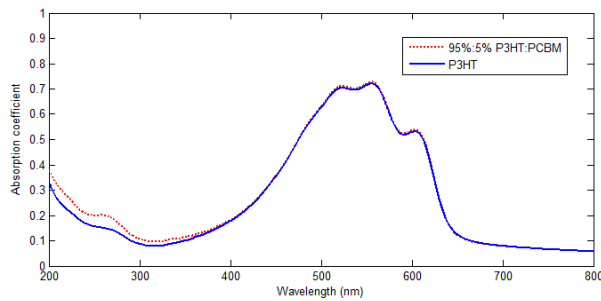


Fig. 2 Comparative dielectric response between the absorption spectra of pure P3HT and the blend 95%:5% P3HT:PCBM measured using UV-VIS spectrophotometer.

A VNA-driven QO transmissometer (Fig. 1 b) measured the scattering parameters across the organic heterojunction from 220-325 GHz [8]. The thickness of the sample was calculated, knowing the density and volume of deposition, as 230 μ m and the mylar film measured as 10 μ m using a micrometer screw gauge. A high power, white, LED, was used as a source of excitation, given the absorption peak of the sample spans the visible spectrum (see Fig. 2). An irradiance of 65mW/cm² in the sample-plane was measured using a photo-diode tuned at 532nm with an area of absorption being 2.27 cm². Fig. 3 shows dispersive estimates of real and imaginary dielectric response of P3HT-PCBM.

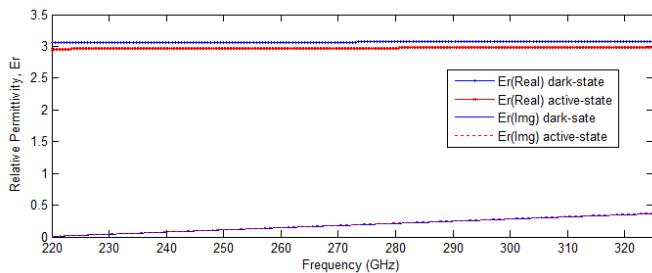


Fig. 3 Dispersive dielectric response of polymer blend (51mg of P3HT:PCBM + 1.5ml chloroform) over the WR-3 waveguide band (220-325 GHz)

A second, lighter, sample, was prepared using 15 mg of P3HT and 0.8 mg of PCBM and 0.5 ml of the high boiling point organic solvent, dichlorobenzene. This was primarily done to achieve a thinner, and hence more even, film, that adheres well to the mylar layer. The measured amplitude and phase of the transmission of the new organic blend (thickness 70 μ m) was used to extract the dielectric values in dark and active states. Fig. 4 co-plots estimates of real and imaginary parts of the complex dielectric response over 220-325 GHz.

III. DISCUSSION OF RESULTS

The measured results for both real and imaginary parts of the permittivity of the 95% P3HT: 5% PCBM organic blend have been analyzed and compared with previously stated values in literature [9]. The ‘active’ imaginary part of the permittivity at active state for both the samples is higher than in off-state, since the conductivity increases with increase in the number of carriers. The polymer blend is observed to be more lossy in the active (on) state with the imaginary part of the permittivity being at a mean value of 0.2 over the measured frequency domain. Additionally, there is a significant difference between the real part of the permittivity in dark and active states. The mean values of the real part of the permittivity in the dark state for both the samples are 3.068

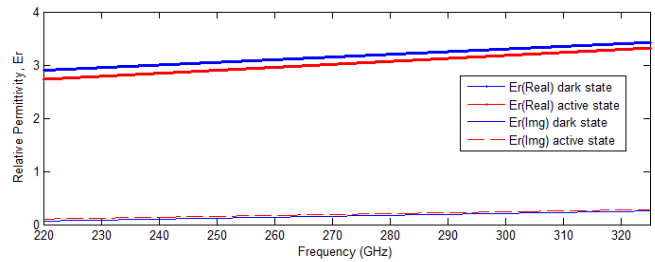


Fig. 4 Dispersive dielectric response of polymer blend (15.8mg of P3HT:PCBM + 0.5ml DCB) over the WR-3 waveguide band.

and 3.1625 respectively. These match with the dark state permittivity of P3HT stated in literature. The average change in permittivity of the first sample (51mg of P3HT:PCBM + 1.5ml chloroform) between active and dark states is measured as 9.5 %. It is observed that the second sample (15.8mg of P3HT:PCBM + 0.5ml DCB) has a greater change in permittivity (13.65 \pm 2 %) than the first. This change in the dielectric of P3HT:PCBM agrees with the statement made about the change in permittivity of P3HT between dark and active states by Tang et al.

IV. SUMMARY

Analysis has been undertaken to measure the active-state change in permittivity of organic heterojunction P3HT:PCBM. Measurement shows evidence of (13.65 \pm 2 %) change in the real part of the permittivity of the organic blend between dark and active states. The dark state permittivity of P3HT-PCBM matches with that of P3HT stated in literature. The change in permittivity of the heterojunction between dark and active states is observed to be slightly higher than the change observed in P3HT. Future work would include measuring the response of a new blend 90%:10% P3HT: PCBM throughout a wider frequency range (75-325 GHz) to observe the effect of increasing PCBM concentration on change in permittivity.

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