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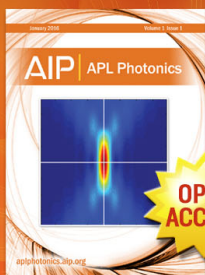
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Electrical characterization of fluorinated benzothiadiazole based conjugated copolymer – a promising material for high-performance solar cells

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Measurements of electrical conductivity, electron work function, carrier mobility of holes and the diffusion length of excitons were performed on samples of conjugated polymers relevant to polymer solar cells. A state of the art fluorinated benzothiadiazole based conjugated copolymer (PBDT_{THD} – DTBTff) was studied and benchmarked against the reference polymer poly-3-hexylthiophene (P3HT). We employed, respectively, four electrode conductivity measurements, Kelvin probe work function measurements, carrier mobility using charge extraction by linearly increasing voltage (CELIV) measurements and diffusion length determination using surface photovoltage measurements. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4939579>]

INTRODUCTION

Recently, polymer solar cells applying fluorinated benzothiadiazole as a motif in conjugated copolymers have exhibited high efficiency and improved stability compared to non-fluorinated benzothiadiazole.¹⁻⁴ The fluorinated PBDT_{THD} – DTBTff copolymer with 2-hexyldecylthiophene side chains on the BDT unit studied here combines electron rich (donor) and electron deficient (acceptor) moieties, see Fig. 1. Structures of this type allow the tuning of the energy levels and absorption properties by controlling the intermolecular charge transferring from the donor to the acceptor.⁵ Successful application of these kinds of materials is based on the charge transport and that is why the knowledge of electrical conductivity, mobility of the charge carriers and exciton diffusion length should be monitored. The major part in this field concentrates on the charge mobility of the polymer which is a crucial parameter for its functionality in photovoltaic devices. Several methods are used to measure charge carrier mobility. They include the time of flight method⁶ which needs a sample with film thickness greater than that used in practical devices and field effect transistor technique⁷ that does not give information on mobility in the bulk. Space charge limited current method is relatively easily applicable to trap-free materials with ohmic contact, while problems arise if there is a barrier for injection from metal electrode to the polymer. Complications are also encountered in the case of traps with various types of distribution.⁸ In the last decade, the transient measurement technique CELIV (charge extraction by linearly increasing voltage) has spread mainly to determine the charge mobility in solar cells.⁹⁻¹² Its advantages are simplicity and the possibility to study samples regardless of their conductivity.

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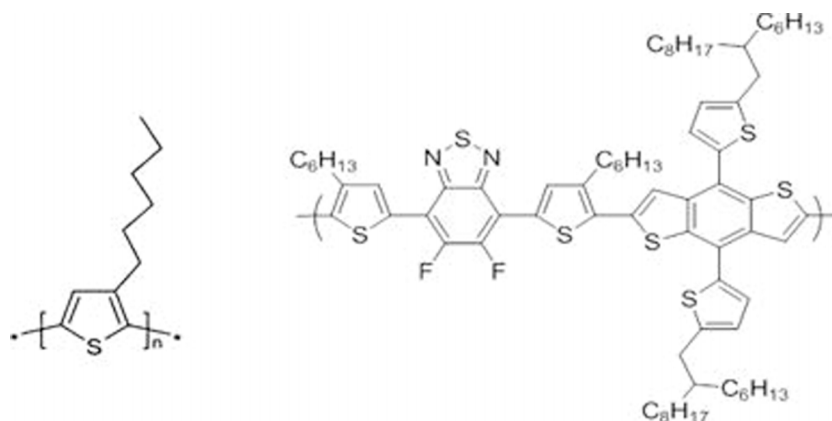


FIG. 1. The chemical structure of the polymers P3HT (left) and PBDT - DTBTff (right).

In this paper, we compare electrical and photoelectrical properties, namely electric conductivity, work function, mobility and exciton diffusion length in PBDT-DTBTff copolymer and in P3HT polymer layers. P3HT has been frequently used in solar cells^{13,14} and PBDT-DTBTff is promising material for reaching elevated power conversion efficiency.² The CELIV method is used for mobility determination.

EXPERIMENT

PBDT-DTBTff and P3HT polymer thin films were deposited on ITO/glass substrates by spin coating from a chlorobenzene solution to give layer thicknesses in the range of 100-300 nm.

Electrical properties were studied by measuring the electric conductivity, work function and mobility of the studied materials. These measurements were carried out in the dark. The surface photovoltage method was employed to obtain the exciton diffusion length. All measurements were performed at room temperature in air to investigate the behavior of the materials which had been prepared in ambient atmosphere.²

Fig. 2 shows the electrical circuit used for the conductivity measurement in the alternating current regime. The measurement was performed at several frequencies to enable approximation of the conductivity to zero frequency. A narrow band amplifier with Keithley 616 electrometer was used as an impedance transformer. Gold electrodes were evaporated and arranged on the top of the samples for current and voltage measurements.

The Kelvin probe was used for measuring the work function of the studied materials. In principle, it is a vibrating capacitor with a reference gold electrode deposited on a glass plate. This electrode is located just above the surface of the sample. The polymer layer deposited on ITO/glass

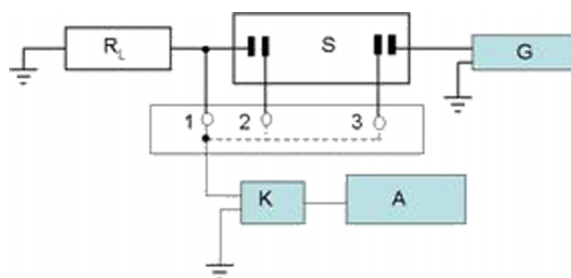


FIG. 2. Conductivity measurement: Current is calculated from the voltage drop on the resistor R_L at point 1, the voltage on the sample is measured at points 2 and 3. K is the electrometer, A is the narrow band amplifier, G is the generator of the alternating signal.

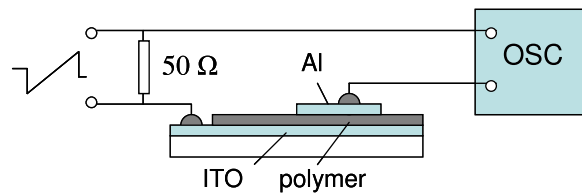
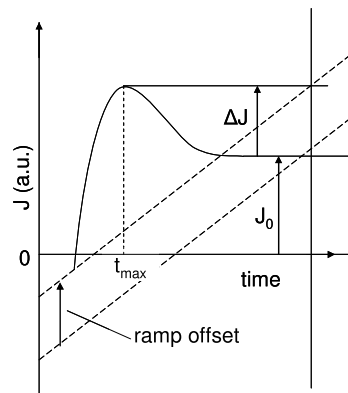


FIG. 3. Experimental set-up for the CELIV measurement.

FIG. 4. Scheme of the dark CELIV measurement. The linear increasing ramps are shown by the dashed lines. For calculation of the mobility the distance between t_{\max} and the intersection of the shifted ramp with the time axis is used for mobility calculation.

serves as a second electrode. When the gold electrode vibrates, alternating voltage appears in the external detection circuit as a consequence of a difference in the work function of the polymer and the gold whose work function was taken as 5 eV.¹⁵ The signal is amplified by a narrow band pass amplifier, which is used as a null detector.

Charge extraction by linearly increasing voltage (CELIV) method was used for measuring the mobility of the polymers under study. The measurement was done in the dark, without illumination. The set-up consists of oscilloscope (OWON DS 7102 V), arbitrary function generator (Agilent 33250 A) and holder with the sample. The sample was provided with one ohmic and one blocking electrode. The idea is to apply a linear increasing voltage pulse (U) to a blocking contact and measure the current response over the time by an oscilloscope. Usually, a light pulse preceding the voltage generates the carriers to be extracted. In our case, the space charge region at Al/polymer Schottky contact is enriched with holes when negative polarity of the voltage ramp is applied to the Al electrode. Majority carriers are extracted in the positive polarity of the ramp. The delay of the charge extraction with respect to the voltage pulse is utilized to determine the mobility. The offset voltage originating in the electrode work functions difference and possibly in externally applied voltage shift the ramp in positive or negative direction. The set-up of the experiment is in Fig. 3 and the schematic response of the CELIV method is in Fig. 4.

To complete the information about important parameters influencing the solar cell efficiency, we measured the surface photovoltage (SPV) to enable extraction of the exciton diffusion length. The arrangement of the experiment is shown in Fig. 5.

The electric field necessary for formation of the SPV was created in the space charge region (SCR) at the Al / polymer interface, while ITO served as an ohmic contact to the polymer. The photovoltage was measured using illumination from the substrate side. The photogenerated excitons diffuse to the SCR where dissociation occurs. The SPV spectra were acquired using low frequency chopped light from the monochromator. The intensity of the light was checked by the thermopile TS100 and the SPV signal was recalculated for constant photon flux density impinging on the sample. Measurement of optical absorption coefficients and reflectance was employed for the SPV measurement evaluation. More information concerning the SPV experiment can be found in Ref. 16.

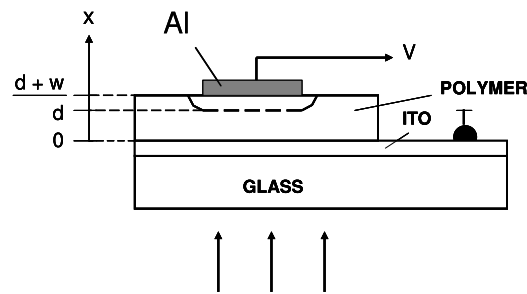


FIG. 5. Arrangement of the SPV measurement: w is the thickness of the space charge region under the Al electrode, d is the thickness of the neutral bulk where diffusion of the photogenerated excitons takes place.

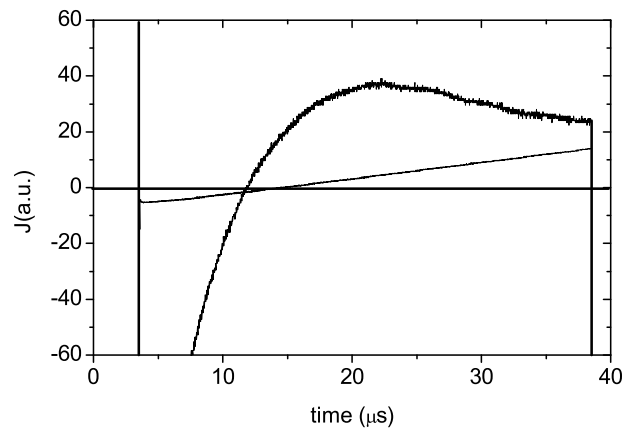


FIG. 6. CELIV curve of P3HT polymer. The straight line shows the shifted ramp used for mobility calculation.

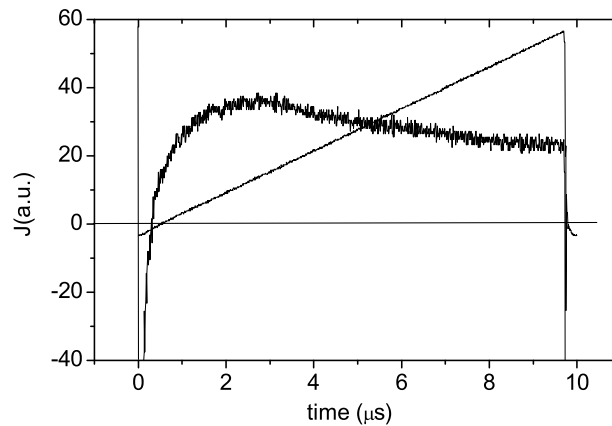


FIG. 7. CELIV curve of PBDT-DTBTff polymer. The straight line shows the shifted ramp used for mobility calculation.

RESULTS AND DISCUSSION

The CELIV measurements were evaluated to obtain the mobility of holes in the P3HT and PBDT-DTBTff polymers. Typical current transients can be seen in Fig. 6 and Fig. 7.

The charge carrier mobility μ was calculated using the relation^{12,17}:

$$\mu = \frac{2d^2}{3At_{\max}^2} \frac{1}{(1 + 0.36\Delta j/j_0)} \quad (1)$$

TABLE I. Measured parameters for calculation of the charge mobility.

Sample	Thickness d (nm)	Voltage slope A (V/s)	$t_{\max}(\mu\text{s})$	$\Delta j / j_0$
P3HT	275	5.7×10^4	4.0	0.55
PBDT-DTBTff	140	6.0×10^5	2.2	0.59

TABLE II. Electrical parameters of P3HT and PBDT-DTBTff. Electrical conductivity and mobility were obtained by resistivity and CELIV measurement, respectively, work function was determined using the Kelvin probe.

Sample	Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Work function (eV)	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
P3HT	3.5×10^{-5}	4.90	4.6×10^{-4}
PBDT-DTBTff	1.3×10^{-5}	4.80	4.0×10^{-5}

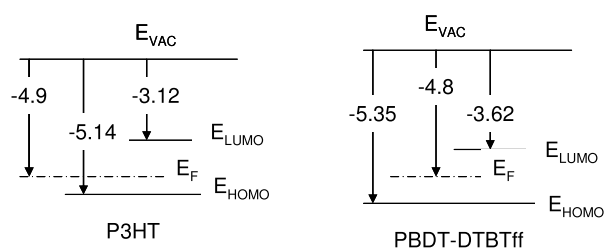


FIG. 8. Energy level diagrams of P3HT and PBDT-DTBTff polymers.

where d is the thickness of the sample, $A = dU/dt$ is the rising speed of linearly increasing voltage U of the ramp, t_{\max} is the time when the current attains its maximum value, j_0 is the capacitive displacement current and Δj is the difference of the current at the maximum and j_0 . Equation (1) holds if $\Delta j \leq j_0$. This condition was fulfilled for all our samples. The thickness of the samples was obtained from AFM measurements. Table I shows these measured parameters used for calculating the charge mobility.

The calculated hole mobility together with the other electrical parameters are in Table II. The relatively low values of mobility may be caused by deep traps. An effective mobility μ_{eff} is measured; it is equal to the mobility of the free holes in the valence band multiplied by the ratio $p/(p + p_T)$,¹⁸ where p is the concentration of the holes in the valence band and p_T is the concentration of the trapped holes.

Cyclic voltammetry yielding the HOMO level of PBDT-DTBTff and the value of the band-gap from optical measurement² were used for energy level diagram construction. HOMO level and the band-gap of P3HT were obtained using the same methods. The work function obtained by the Kelvin probe experiment enabled the Fermi level determination. Fig. 8 shows the energy level diagram of the P3HT and the PBDT-DTBTff samples.

The band-gap of the P3HT (2.02 eV) agrees well with that reported in the literature^{19,20} and the HOMO level (-5.14 eV) falls into the published range (-5.1 to -5.2) eV.^{21,22} The mobility of P3HT $\mu = 4.6 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which is here measured in the diode configuration, is in agreement with the published data.²³⁻²⁵ The mobility measured on fresh samples is about one order of magnitude higher than that of PBDT-DTBTff. It is probably caused by presence of traps which can be seen in the spectrum of the absorption coefficients measured in the region of 750 nm – 1200 nm (not shown). While we have obtained practically zero in the case of P3HT samples quite high values were measured (about 8000 cm^{-1}) for PBDT-DTBTff.

However, after one year the mobility of the P3HT decreased to $1.4 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, indicating degradation effects. As the samples were stored in air, oxidation is very probable. Oxygen induces degradation and decreases mobility of P3HT as it is known from literature (Refs. 23, 26, 27). We could not yet measure PBDT-DTBTff samples after one year (they are relatively new) but after 6 months the mobility was not lower as compared with the fresh samples.

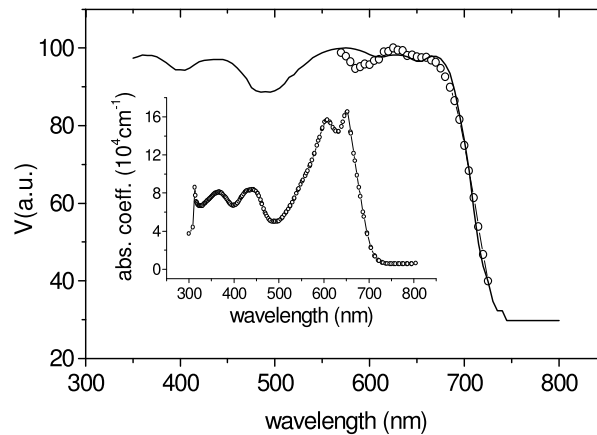


FIG. 9. Normalized photovoltage spectra of PBDT-DTBTff. Full line - theory fitted to the experimental points with the parameters: $w = 40$ nm, $d = 90$ nm, $L = 12$ nm. The inset shows the spectral dependence of absorption coefficient.

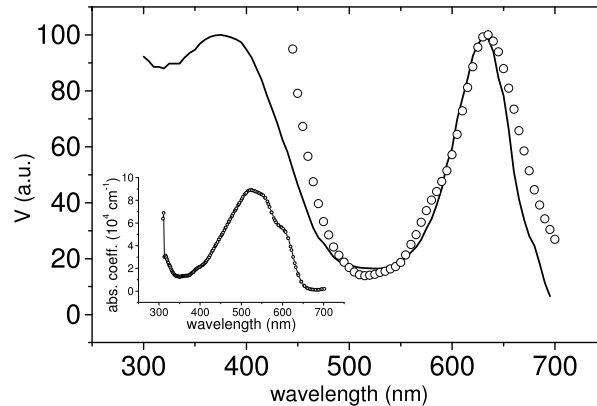


FIG. 10. Normalized photovoltage spectra of P3HT. Full line - theory fitted to the experimental points with the parameters: $w = 20$ nm, $d = 310$ nm, $L = 6$ nm. The inset shows the spectral dependence of absorption coefficient.

The free carrier density cannot be obtained using the conductivity and mobility measured by CELIV method (the Fermi level E_F moves during the application of the voltage ramp²⁸). Exciton diffusion length was determined using the approach briefly described in Appendix and more precisely presented in Ref. 29. Figs 9 and 10 show the experimental and fitted theoretical photovoltage spectra of PBDT-DTBTff and P3HT samples, respectively. The spectral dependences of the absorption coefficients are in the insets. Fitting the theoretical curves among others provides diffusion length L , thickness of the bulk d and thickness of the SCR w . The exciton diffusion length in PBDT-DTBTff is 10-12 nm, which is two times greater than that of P3HT, which is 5-6 nm.

Different forms of the curves in these figures are the consequence of a different ratio between the distance of the point where exciton is generated and the boundary of the SCR where its dissociation occurs. The higher the absorption, the longer the distance (see Fig 5). The spectrum of the P3HT samples (Fig. 10) shows a minimum at the wavelengths corresponding to the maximum in absorption spectrum. The thickness of these samples is quite large and the excitons have to pass a long path to reach the SCR. With short diffusion length this means high losses of the excitons. A different situation occurs for the PBDT-DTBTff samples. The SPV spectra in the red region approximately follow the absorption because the diffusion length does not differ too much from the thickness of the bulk and thus the losses of the excitons during diffusion are low. Problems come at wavelengths below about 600 nm where the experimental curve increases and does no longer follow the theory. This discrepancy will be further examined.

CONCLUSION

Electrical properties of the fluorinated benzothiadiazole based copolymer PBDT-DTBTff were studied and compared with the results obtained for the polymer P3HT, a benchmark within organic photovoltaics. Electrical conductivity was comparable in both polymers, being of the order of $10^{-5} \Omega^{-1} \text{ cm}^{-1}$. Mobility of holes in P3HT is higher as compared with that in PBDT-DTBTff, due to higher concentration of traps in PBDT-DTBTff. But the mobility in P3HT shows a decrease with time, which indicates a low photochemical stability very probably due to the influence of oxygen. PBDT-DTBTff material exhibits a quite long diffusion length (12 nm) and a wide region of spectral response extended to 700 nm in the long wavelength part. Compared to the polymer P3HT this copolymer shows higher absorption coefficients in whole measured wavelength region. Together with the results of the photochemical stability² it can be concluded that PBDT-DTBTff is promising for polymer solar cells production.

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APPENDIX

Our approach to the surface photovoltage (SPV) method²⁹ was employed to obtain the exciton diffusion length. Here we present the derivation only briefly. First, the diffusion equation for motion of the excitons generated in the bulk of the sample is solved with the boundary conditions (see Fig 5):

- 1) $\Delta n(d) = 0$
- 2) $D \frac{d\Delta n}{dx} \Big|_{x=0} = s\Delta n(0)$

where Δn is the exciton concentration, D is the diffusion coefficient, s is the surface recombination velocity. As a result, we have the Δn needed for the calculation of diffusion current from the bulk. The respective current density $J_b = eD d\Delta n/dx \Big|_{x=d}$ uses the absorption coefficients and the reflectance and it contains in itself the diffusion length, the thickness of the bulk and the thickness of the space charge region (SCR).

The excitons generated in the SCR are dissociated and the charge of electrons and holes is multiplied by a factor $G \epsilon < 0, 1 >$. Losses by recombination and/or incomplete dissociation can be included in this way. By integration of the charge photogeneration rate over the thickness w of the SCR the current density from this region is:

$$J_s = a_1 G \exp(-\alpha d) \int_0^w \alpha \exp(-\alpha x) dx + a_2 G \int_0^w \alpha \exp(-\alpha x) dx$$

Where α is the absorption coefficient, d is the thickness of the bulk, a_1 and a_2 represent relations for the case of multiple reflections.³⁰

The total photocurrent density J is a sum of both these contributions:

$$J = J_b + J_s$$

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