Organic Electronics 22 (2015) 62–68

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

# Charge carrier mobility of the organic photovoltaic materials PTB7 and $PC_{71}BM$ and its influence on device performance

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ARTICLE INFO

Article history:
Received 21 December 2014
Received in revised form 9 March 2015
Accepted 9 March 2015
Available online 11 March 2015

Keywords:
Time of flight
Temperature
Efficiency
Bimolecular recombination
Trap-assisted recombination

## ABSTRACT

The mobility is an important parameter for organic solar cell materials as it influences the charge extraction and recombination dynamics. In this study, the time of flight technique is used to investigate the charge mobility of the important organic photovoltaic materials $PC_{71}BM$, PTB7 and their blend. The electron mobility of $PC_{71}BM$ is in the region of $1 \times 10^{-3}$ cm$^2$/Vs for the neat fullerene film, and has a positive electric field dependence. At room temperature the hole mobility of PTB7 is $1 \times 10^{-3}$ cm$^2$/Vs for the neat film and $2 \times 10^{-4}$ cm$^2$/Vs for their blend. The hole mobility of the blend reduces by a factor of a thousand when the sample is cooled from room temperature to 77 K. This finding is compared with the device performance of efficient $PTB7{:}PC_{71}BM$ solar cells for varying temperature. At 77 K the solar cell efficiency halved, due to losses in fill factor and short circuit current. Bimolecular and trap-assisted recombination increase at low mobility (low temperature) conditions, whereas at high mobility conditions the open circuit voltage reduces. The power conversion efficiency as a function of temperature has a maximum between 260 K and 295 K, revealing an optimized mobility at room temperature.

## 1. Introduction

The polymeric donor material PTB7 (poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-(2-ethylhexy)carbonyl]thieno[3,4-b]thiophenediyl]]) has attracted great interest in recent years due to its high performance in bulk heterojunction solar cells. Devices of PTB7 blended with $PC_{71}BM$ ([6,6]phenyl C71 butyric acid methyl ester) exhibit a high fill factor (FF) of up to 72% and external quantum efficiency (EQE) of 80% [1]. Both of these parameters are strongly influenced by the charge transport properties of the active layer. Accordingly this paper has two aims. The first is to report mobility measurements of these important and widely used solar cell materials. The second is to explore the influence of the mobility on device operation and charge recombination.

The main steps of operation in an organic solar cell are: light absorption, charge separation and charge transport to the electrodes. During charge transport of electrons in the acceptor phase and holes in the donor phase two types of recombination can occur which reduce the power conversion efficiency. Bimolecular recombination happens after an encounter between an electron and a hole in the material. This process is generally described by Langevin theory where the recombination rate $R_B$ depends on the mobility and density of electrons and holes [2,3],

$$R_B = \frac{e}{\epsilon}(\mu_e + \mu_h)(np - n_i^2) \tag{1}$$

where $\epsilon$ is the dielectric constant ($\epsilon_0 \epsilon_r$), $e$ the elemental charge, $\mu_e$ and $\mu_h$ are the electron and hole mobility, $n$ the electron density, $p$ the hole density and $n_i$ the density of intrinsic charge carriers. Since electrons and holes are created in pairs, $R_B$ depends quadratically on the density of electrons stored in the device, $n^2$, which is generally much larger than the density of intrinsic charge carriers. Monomolecular recombination occurs when one charge carrier encounters an occupied trap state of immobile charge with the opposite sign. It is often described by a Shockley–Read–Hall (SRH) mechanism and depends on the density of trap states and is proportional to the density of mobile charge carriers, $n$ [4,5]. The SRH recombination is given by the density of electron and hole trap states ($n_{\text{traps}}$, $p_{\text{traps}}$) and the lifetime of the trap state ($\tau_e$, $\tau_h$) and the rate constant is given by [6]

$$R_{\text{SRH}} = \frac{np - n_i^2}{\tau_e(n + n_{\text{traps}}) + \tau_h(p + p_{\text{traps}})} \tag{2}$$

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http://dx.doi.org/10.1016/j.orgel.2015.03.013
1566-1199/

The mobility in disordered organic semiconductors is also influenced by trap states and the temperature, it decreases with decreasing temperature and increasing trap density [7].

To achieve a high external quantum efficiency of the solar cell, charges must be extracted faster than they recombine. The maximum extraction time is the device thickness divided by the drift velocity i.e. $d/\mu E$ where μ is the lowest mobility of electrons or holes, which should be similar, and $E$ is the electric field.

$$\frac{d}{\mu E} < \frac{n}{R_B + R_{SRH}} \tag{3}$$

The above formalism shows the strong influence of the charge carrier mobility on the operation of photovoltaic devices. It is a crucial parameter for optimized device efficiencies and the time of flight (TOF) technique is the most accurate way to determine it. This paper reports the charge mobility for the important materials $PC_{71}BM$, PTB7 and their blend, measured by TOF with its electric field and temperature dependence. Although the influence of mobility on device operation has been explored theoretically [8–11], an experimental relation to the solar cell performance has not been deeply studied. Only recently a direct relation of mobility to device performance has been drawn in small molecule based solar cells for a variety of donor and acceptor blends and an increase of fill factor with increasing hole mobility was observed [12]. To further optimize devices it is important to know what role the mobility of the materials plays. For that, device characteristics were studied at low temperature (low mobility) and high temperature (high mobility) conditions and the associated recombination processes identified.

## 2. Materials and methods

PTB7 was purchased from 1-Material and $PC_{71}BM$ from Solenne. Neat films of $PC_{71}BM$ for TOF measurements were prepared from a solution of 49 mg/ml of $PC_{71}BM$ in tetrachloroethane. Films of neat PTB7 and blends of PTB7:$PC_{71}BM$ (1:1.5) were prepared from solutions of in total 40 mg/ml in 1,2-dichlorobenzene. For the blend 3 vol% diiodooctane was added to the solution. Glass substrates with a 4 mm stripe of ITO were cleaned with acetone, propan-2-ol and plasma ashing. For samples of $PC_{71}BM$, $MoO_3$ of about 8 nm thickness was thermally evaporated onto the ITO substrates, whereas for PTB7 and PTB7:$PC_{71}BM$ samples, PEDOT:PSS was spin coated instead and dried at 120 °C for 10 min. The active layer was then solution cast and dried overnight in a nitrogen glove box. The cathode of 15 nm calcium and 15 nm aluminum was thermally evaporated to create a semi-transparent contact. Three pixels with an area of 8 $mm^2$ were defined by the overlap of the anode and cathode. The film thickness was determined individually for each pixel by a surface profilometer after electrical characterization of the device.

Solar cells were fabricated in a similar way on PEDOT:PSS, using solutions of PTB7:$PC_{71}BM$ of 25 mg/ml concentration, spin coated at 1000 rpm to give films of 80 nm thickness. The aluminum thickness was 100–150 nm. Solar cells were encapsulated with a UV-curing epoxy and a glass slide.

TOF measurements were performed in a vacuum cryostat at less than $10^{-4}$ mbar pressure. The sample was excited by a tuneable nitrogen pumped dye laser using a wavelength of 640 nm for PTB7 or 337 nm for $PC_{71}BM$ and PTB7:$PC_{71}BM$ with a pulse-duration of 500 ps. The film thickness of the solution cast samples was much higher than the absorption depth, calculated from the absorption coefficient. Thus the condition that charges are generated in a thin sheet compared to the total layer thickness was clearly fulfilled. The laser power was attenuated so that the amount of extracted charge was small enough to avoid space charge effects but large enough to provide good signal to noise. For electron mobility measurements, the sample was excited from the ITO electrode and for hole mobility measurements through the calcium/aluminum electrode. In both cases positive bias was applied to the calcium/aluminum electrode, operating the device in reverse direction, to avoid charge injection. The photocurrent was measured with a digital storage oscilloscope. The temperature was regulated by the evaporation rate of liquid nitrogen and a heat source.

Solar cells were first measured under a class A, Sciencetech solar simulator and the intensity calibrated with an ORIEL reference cell with KG5 filter. The spectral mismatch factor was close to unity (0.995) for PTB7:$PC_{71}BM$ and not corrected for. An aperture of the same size as the pixel was used to avoid contribution from stray light outside the device area. The solar cell was then transferred into the cryostat and illuminated in a range of intensities from a collimated white-light LED. We took one sun illumination to be the LED intensity which gave the same current as measured under the simulator. The relative intensity of the LED was calibrated for linearity using a photodiode.

To obtain the EQE spectrum, the short circuit current of the solar cells was measured under monochromatic illumination and compared with a calibrated photodiode. Due to reflections on the cryostat window and the beam being larger than the device size an absolute value of EQE was not determined. Absorption of a PTB7:$PC_{71}BM$ film, spin coated onto a quartz substrate, was measured with the cryostat placed in the beam path of a Cary 300 spectrometer.

## 3. Results and discussion

### 3.1. Hole mobility of PTB7

The time of flight measurement technique is a widely used method for determining mobility and has several advantages over other methods. It measures the mobility perpendicular to the substrate, at low charge density, has simple data analysis protocols and has the advantage that electron and hole mobility can be distinguished in the same device configuration, and their dependence on the applied electric field determined. In neat PTB7, photocurrents with a pronounced kink were observed, which is in contrast to a recent publication by Philippa et al. who found very dispersive and featureless TOF transients [13]. An example of a photocurrent transient is shown in Fig. 1(a). The transit time was obtained on logarithmic plots by the intersection of a linear fit to the plateau and tail of the curve [14].

The hole mobility of PTB7 is approximately $1 \times 10^{-3}$ $cm^2/Vs$ at an applied electric field of $1.1 \times 10^5$ V/cm ($E^{0.5} = 335$ $(V/cm)^{0.5}$) and a film thickness of 8.3 μm. The effect of electric field on the mobility was measured and the results are shown as a Poole–Frenkel plot [15] in Fig. 1(b) and reveal only very weak field dependence. Our value of the hole mobility in PTB7 is slightly higher compared to results found by space charge limited current (SCLC) measurements, which were reported in the range $2–5.8 \times 10^{-4}$ $cm^2/Vs$ [16–19]. The TOF mobility of PTB7 is almost one order of magnitude higher than that of P3HT for which reported values are about $2 \times 10^{-4}$ $cm^2/Vs$ [20].

### 3.2. Electron mobility of $PC_{71}BM$

Next we performed studies of the electron mobility of $PC_{71}BM$ by TOF. Mobility measurements of fullerenes by TOF so far were mainly done indirectly, either in blends with other conjugated polymers or an insulating matrix, because of the rather poor film quality of neat fullerene films [21]. The blend morphology and