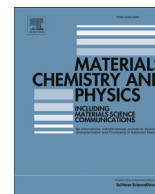




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# The effect of polymer solar cell degradation on charge carrier dynamics in benzodithiophene-diketopyrrolopyrrole polymers

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## HIGHLIGHTS

- Photo-degradation in a couple of poly(benzodithiophene-diketopyrrolopyrrole) polymers have been studied.
- Charge extraction measurements reveal increased number of trapped charge carriers with progressive degradation.
- Bulk charge carrier mobility is found to be unchanged through the process of degradation.

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## ABSTRACT

Degradation in polymer based organic solar cells still remains poorly understood despite prominent research efforts in recent years. In this work, the impact of photostability and documented morphological evolution of a couple of poly(benzodithiophene-diketopyrrolopyrrole) polymers in their blends with phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) are investigated by a combination of charge extraction techniques. Photo-induced charge carrier extraction by linearly increasing voltage (photo-CELIV) and integral-time of flight (TOF) methods are employed to determine charge carrier mobility and recombination at various stages of photo-degradation in the absence of air. We report the progressive formation of deeper trap states as crucial outcome of photo-degradation within these blends as deduced from our measurements.

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## 1. Introduction

The photostability of organic photovoltaic (OPV) devices has been a primary hurdle to their commercialization for over a decade. Significant progress has been made for their stabilization employing inverted device architectures [1,2] and expensive barrier layers [3,4]. In some cases, such as the ubiquitous poly-3hexylthiophene (P3HT) and its blends with PCBM, stability for thousands of hours have been achieved [5,6]. The field of OPV chemistry offers many material strategies to achieve high performance ranging from polymers to small molecules. Unfortunately, each of these materials are often unique in their device stability, each having different

paths for their degradation which can include photochemistry [7,8], morphological ripening [9,10], reaction with molecular oxygen, interface migration/reaction [11,12] and delamination [13,14]. Building a detailed understanding of these processes is essential for laying a path for the eventual commercialization of OPV technology.

Among the several degradation pathways, morphological ripening of the blend phase is an inherent problem that cannot be avoided by limiting water or oxygen ingress through device engineering or effective encapsulation. The impact of AM1.5 solar radiation ageing on charge carrier transport properties is essential to understand the processes taking place during degradation and is not yet extensively studied. Of the techniques available, only photo-CELIV (charge extraction by linearly increasing voltage) is able to extract charge carrier information on fully constructed and operational OPV devices [15,16], allowing these measurements to be

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made during degradation analysis. Charge carrier analysis of OPV devices is crucial to being an understanding of essential device properties such as charge carrier density, charge transport and recombination dynamics. In this study, extraction current transients are employed to obtain charge carrier transport properties of OPV devices containing two different poly(benzodithiophene-*alt*-diketopyrrolopyrrole) (pBDT-*alt*-DPP) derivatives in blends with PCBM. This investigation follows from our previous study where it was shown that device degradation resulted from a combination of fast PCBM dimerization followed by slow PCBM crystallization [17]. Herein the two derivatives differing only in side chain (Fig. 1) with remarkably different photo-thermal evolution of photovoltaic properties were studied with respect to charge carrier transport during the course of degradation. Photo-generated charge carriers were analysed by photo-CELIV and integral time of flight (iTOF) techniques. Measurements were carried out on glass-encapsulated devices, which were exposed to AM 1.5 illumination in ambient conditions for as long as 80 h, data points being collected every 20 h.

## 2. Experimental

### 2.1. Materials

The pBDT-*alt*-DPP polymers were prepared according to previous reports [17]. PCBM was obtained from Nano-C Inc. and used as supplied. Zinc acetate dihydrate (Aldrich), dimethylsulphoxide (Aldrich) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) Clevis HTL Solar SCA 246-9 (Heraeus) were used as supplied.

### 2.2. Device fabrication

Inverted structure devices were fabricated on 13  $\Omega/\text{cm}^2$  photolithography patterned ITO. The zinc oxide transport layer was formed by spin-coating a solution of zinc acetate dihydrate in dimethylsulphoxide at 160 g/L at 4000 rpm for 10 s followed by a 5 min thermal anneal at 300 °C. The active layer was deposited by blade coating. On top of the active layer a uniform layer of PEDOT:PSS was spin-coated at 1100 rpm for 130 s. The silver top electrode was applied by vacuum deposition at  $2 \times 10^{-6}$  mbar at

1–5 Å/s. The devices were subsequently encapsulated with a top glass cover slide containing a 120  $\mu\text{m}$  cavity in the center of the slide. The outer edge of the cover slide was sealed using UV curing epoxy. The devices were exposed to AM 1.5 from a Newport 94082A Solar Simulator and data was collected using a sourcemeter (Keithley 2400) connected through a switch system (Keithley 2750).

### 2.3. Measurements

Photo-CELIV and TOF measurements were carried out using a 0.1 mJ, 4.3 ns pulsed laser at 700 nm wavelength (EKSPLA NT 340) as illumination source, voltage pulse was applied from a function generator (Tektronix AFG 3011) and corresponding current transients were sampled and recorded using an oscilloscope (Tektronix DPO 4054B). The probe wavelength was chosen to attain substantial photo-excitation according to the absorption spectrum (Fig. S1). Neutral density calibrated filters were used to vary the illumination intensity and the delay time was controlled by the function generator.

While Photo-CELIV data was primarily used to determine mobility, high intensity integral TOF was employed to study the recombination and hence to obtain the Langevin recombination coefficient. Due to the large RC time constant (small thickness and large contact area) the TOF measurements were limited to integral regime and volume photo generation.

In photo-CELIV photo-generated charges are extracted from the active layer using a linearly increasing voltage pulse at a variable delay time  $t_{del}$  after photo-excitation. The drift mobility of the carriers is determined from the time to reach maximum of the extraction current  $t_{max}$ , using the following equation:

$$\mu = \frac{2d^2}{3At_{max}^2} \quad (1)$$

which is valid in low conductivity materials ( $\Delta j \leq j_0$ ) for bulk photogeneration. Here  $d$  is the thickness of active layer,  $A$  is the voltage rise speed,  $\Delta j$  is the extraction current and  $j_0$  is the charging current of the sample capacitance. It has been acknowledged that the CELIV peak is influenced by both carriers and hence the average mobility is obtained. However, in cases where the electron and hole mobilities are highly unbalanced, it could be argued that the obtained mobility is predominantly of the faster carrier [18]. Integrating the CELIV transients at different delay times also provides us with relevant information regarding photogenerated charge carrier density dynamics in microseconds or longer time scales.

Integral TOF with bulk photogeneration is employed as a complementary technique, which has been reportedly used to determine the bimolecular recombination coefficient  $\beta$  in organic solar cells [19]. The saturation of integral TOF signal with increasing excitation light intensity indicates that the recombination in the blend being predominantly bimolecular (or higher order). Knowledge of the extraction time of charges in the reservoir provides insight into the rate of bimolecular recombination.

## 3. Results and discussion

### 3.1. Photovoltaic characteristics

The current density – voltage (J-V) dependencies of glass-encapsulated devices based on the two different derivatives were recorded up to 80 h of AM 1.5 illumination and the extraction current transient measurements were simultaneously carried out. The pristine devices were optimised to yield power conversion

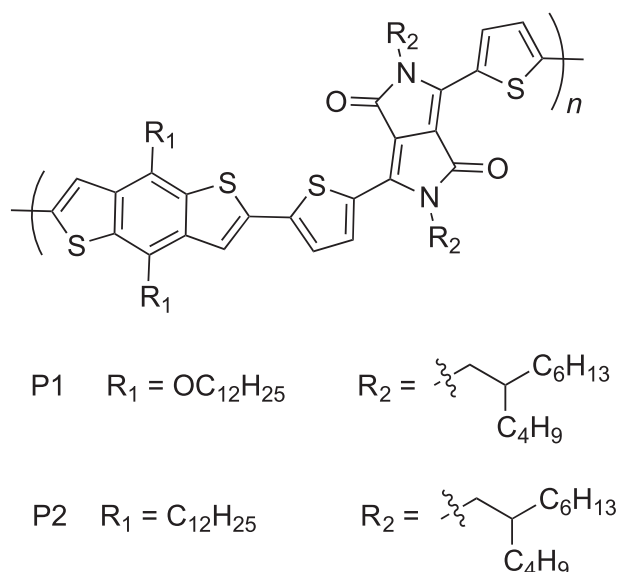


Fig. 1. Structure of pBDT-*alt*-DPP derivatives used in this study.

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