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Quantifying space charge accumulation in organic bulk heterojunctions by nonlinear optical microscopy

J.D. Morris [a,1], Timothy L. Atallah [b], Heungman Park [b], Zien Ooi [c], Ananth Dodabalapur [d], X.-Y. Zhu [b,*]

[a] Department of Chemistry and Biochemistry, University of Texas, Austin, TX 78759, USA
[b] Department of Chemistry, Columbia University, New York, NY 10027, USA
[c] Institute for Materials Research and Engineering, Agency for Science, Technology, and Research, 3 Research Link, Singapore 117602, Singapore
[d] Department of Electrical Engineering, University of Texas, Austin, TX 78712, USA

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ABSTRACT

In this work, we apply electric field induced second harmonic generation microscopy to directly observe and quantify space charge accumulation in operating organic bulk heterojunction photovoltaic cells comprised of poly(4,4-dioctyldithieno(3,2-b:2′,3′-d)silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl) (PSBTBT) mixed with phenyl-C61-butyric acid methyl ester (PCBM). We adjust the effective electron and hole mobility within these blends by altering the relative composition of PSBTBT and PCBM, and observe dramatic shifts in space charge accumulation. The PSBTBT rich device shows strong electron accumulation (2.8×10^{14} e^-/cm^3) and the PCBM rich device shows strong hole accumulation (5.5×10^{14} h^+/cm^3).

1. Introduction

A significant mismatch between electron and hole mobilities in a photoconductor or photovoltaic cell is known to result in space charge accumulation and deviation from charge neutrality during device operation [1]. Such space charge regions can give rise to a fundamental limit on photocurrent, thus reducing device efficiency by increasing charge carrier recombination [2,3]. In their seminal analysis [1], Goodman and Rose provided a number of quantitative predictions on device characteristics in the space charge limited regime, including the dependence of photocurrent (J_{ph}) on the charge generation rate (G): $J_{ph} \propto G^{3/4}$. Blom and coworkers provided experimental evidences for these predictions using the model system of organic donor/acceptor bulk heterojunctions (BHJs) [2] and showed how space charge accumulation led to fundamental limits in photocurrent in organic photovoltaics (OPVs) with considerable mismatch in charge carrier mobilities. Most experimental studies to date on space charge accumulation have relied on integrated current–voltage measurements [4–6], but there are also limitations on these common approaches because photocurrent can be affected by a variety of factors such as charge carrier recombination [7] and the presence of contact resistance [8]. An effective approach to overcome these limitations is to directly determine the spatial distributions of electric fields in operating devices. We demonstrated recently such an approach using electric field induced second harmonic generation (EFISH) microscopy [9]. Compare to the successfully demonstrated scanning probe techniques in

Abbreviations: EFISH, electric field induced second harmonic generation; OPV, organic photovoltaic; PSBTBT, poly(4,4-dioctyldithieno(3,2-b:2′,3′-d)silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl); PCBM, phenyl-C61-butyric acid methyl ester; BHJ, bulk heterojunction; LBHJ, lateral bulk heterojunction.

* Corresponding author.
E-mail address: xyzhu@columbia.edu (X.-Y. Zhu).
[1] Present address: Department of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Drive, Atlanta, GA 30332, USA.

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mapping electrostatic and photocurrent distributions in organic devices [10,11], the EFISH microscopy gives lower spatial resolution but offers the advantage of contact-free imaging in operating devices.

Here we apply EFISH microscopy to directly observe and quantify space charge accumulation in active organic bulk heterojunction devices comprised of phenyl-C61-butyric acid methyl ester (PCBM) mixed with poly(4,4-dioctyldithieno(3,2-b:2′,3′-d)silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl) (PSBTBT). PSBTBT is a low bandgap polymer optimized for the solar spectrum [12]. We use the lateral bulk heterojunction (LBHJ) geometry [13], which is not optimal for high solar-to-electric power conversion efficiency, but allows us to directly access the active region. We use EFISH microscopy to determine the spatial distributions of electric fields in LBHJ devices to provide unambiguous information on space charge accumulation. These experimental findings will be compared with numerical simulations by Ooi et al. on space charge accumulation within LBHJ devices using a drift–diffusion model [14,15].

2. Material and methods

2.1. Sample preparation

We used photolithography to pattern both the aluminum (Al) cathodes (50 nm thick) and gold (Au) anodes (50 nm thick) on a glass substrate for the fabrication of LBHJ devices. The inter-electrode spacing was 20 μm (shown in Fig. 1b). After a short etch in phosphoric acid and an acetone rinse, we spin-coated each BHJ thin film at 800 rpms for 60 s resulting in a film thickness of 60 nm as confirmed by ellipsometry. Each film was comprised of PSBTBT:PCBM in varying weight ratios of 2:3, 3:1 and 1:3, which we spin-coated from a solution of 12 mg/ml PSBTBT and 18 mg/ml PCBM, 22.5 mg/ml PSBTBT and 7.5 mg PCBM, and finally, 7.5 mg PCBM and 22.5 mg/ml PCBM respectively, all in chlorobenzene. After spin-coating, we heated the PSBTBT:PCBM films to 80 °C for 30 min to remove any remaining chlorobenzene [16]. Finally we encapsulated the LBHJs using a microscope coverslip and optical epoxy, which was cured at 125 °C for 10 min. All device preparation took place in a dry nitrogen environment.

PSBTBT is a crystalline polymer and its blend with PCBM has been extensively investigated before [12,17,18]. The high performance of this blend in OPVs has been attributed to not only near optimal absorption of the solar spectrum but also high hole mobility and reduced charge carrier recombination. Structural characterization showed a 26% solubility of PCBM in PSBTBT [19]. For the three compositions used here (PSBTBT:PCBM = 3:1, 2:3, and 1:3), we expect, in addition to crystalline PSBTBT and mixed PSBTBT and PCBM domains, PCBM domains of increasing sizes.

2.2. EFISH microscopy

All microscopy images were taken in the transmission mode. The fundamental beam at 1060 nm (pulse width: 120 fs; rep-rate: 76 MHz; pulse energy: 2 nJ) was generated by an optical parametric oscillator (Coherent Mira-OPO) pumped by a Ti:sapphire oscillator (Coherent Mira HP) (Fig. 1a). This fundamental beam was focused to a diameter of 80 μm by an f = 10 cm lens. The EFISH signal at 530 nm was collected by a microscope objective (Mitutoyo 20×) and, after passing through appropriate filters, imaged on an EM-CCD camera (Andor Technology 897E). In order to take a typical EFISH image, we applied a fixed voltage (V_0 = 200 V) and integrated the second harmonic intensity for 30 s. We chose this voltage in order to generate an electric field strength typical in OPVs and also because simulations suggest the appearance of distinct regions of space charge accumulation near this voltage [14].

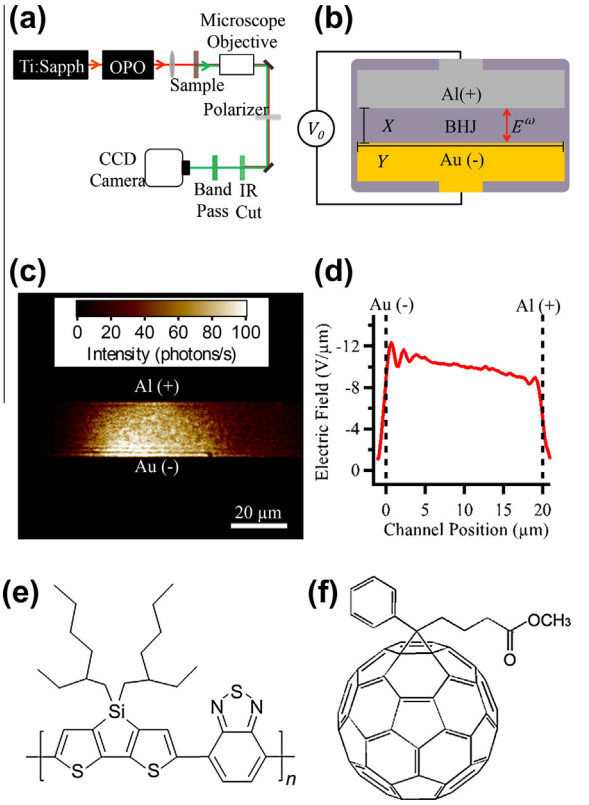

Fig. 1. (a) A schematic of the optical layout. (b) A schematic of the LBHJ device geometry. The red line represents the polarization of the incident electric field. The channel length in the x direction is 20 μm while the electrode width in the y direction is 1 mm. (c) An EFISH image of 2:3 PSBTBT:PCBM at 200 V. (d) An average of many line profiles across the image in 1c in the x direction which has been calibrated to give the electric field strength. Molecular structures of (e) PSBTBT and (f) PCBM. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. EFISH fundamentals

EFISH is a special case of second harmonic generation (SHG) where the efficiency of converting two photons at frequency ω to one photon at frequency 2ω depends on the strength of the electric field present [20]. The second harmonic response from the type of samples we are probing is given by [9]: