



# Improved performance of polymer photodetectors using indium–tin-oxide modified by phosphonic acid-based self-assembled monolayer treatment



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## ABSTRACT

For organic photodetectors (OPDs), in order to realize high incident-photon-to-current conversion efficiency (IPCE) and high on/off ratio, the characteristics of hole-only devices and polymer photodetectors with indium–tin-oxide (ITO) modified by phosphonic acid-based self-assembled monolayer treatment in a short time are investigated. 1H,1H,2H,2H-Perfluorooctanephosphonic acid (FOPA) treatment results not only in lowering of the injection barrier at the ITO/organic layer interface but also in the lowering of the contact resistance between ITO and the organic layer. An OPD based on a blend of a donor, poly(9,9-dioctylfluorene-co-bithiophene) (F8T2), and an acceptor, fullerene derivative [6,6]phenyl-C61-butyric acid methyl ester (PCBM) with FOPA treatment exhibits blue-light sensitivity and IPCE of approximately 75% at  $-4$  V. For the F8T2:PCBM device with FOPA, the IPCE is improved, and the dark current hardly increases. F8T2:PCBM device with FOPA treatment exhibits high on/off ratio, wide detector dynamic range and cut-off frequency of more than 10 MHz under reverse voltage.

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## 1. Introduction

Solution processing is attractive from the viewpoint of it being a simple fabrication process for large-area devices. Organic devices utilizing conjugated polymers have attracted considerable interest because of their advantages for large-area device fabrication. Fullerene derivatives doped in several conducting polymers act as effective quenchers and electron acceptors, and this photophysics is known as ultrafast photoinduced charge transfer [1–3].

Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) blends have been studied for organic bulk heterojunction photovoltaic cells because of high hole mobility and a broad absorption spectrum, and high photoelectric conversion efficiencies have

consequently been achieved [4]. An organic photodetector (OPD) is an organic device with photoelectric conversion characteristics [5–8]. Important factors for organic solar cells are absorption wavelength, filling factor, open circuit voltage, and short-circuit current. On the other hand, the electrical characteristics under reverse bias, color sensitivity, on/off ratio, and frequency response must also be evaluated for OPDs.

OPDs have been the subject of extensive research owing to their several advantages, including light weight, flexibility, and low-cost fabrication. Furthermore, we can select the absorption wavelength of the OPDs by choosing organic materials with suitable absorption wavelengths. It is thus easy to realize color sensitive photodetectors [9–11]. Fluorene-type polymers have emerged as an important class of conducting polymers due to their efficient emission, high stability, and relatively high mobility [12–16]. They can be imparted various absorption

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wavelengths by appropriately selecting side-chains or copolymers, and they are promising materials for large-area optoelectronic devices such as OPDs. Printable photodetectors have huge potential in applications such as large-area photodetector arrays, scanners [17–20]. OPDs also show high potential for use in future information technology systems, especially for signal processing and optical sensing systems with flexible devices [6,21–24].

Device performance is influenced by the donor–acceptor interface. In addition, contact formation between an anode and the organic layer is one of the key issues in the development of organic devices. Surface treatment of electrodes using self-assembled monolayers (SAMs) could be an effective method to improve the performance of organic devices [25–29]. In general, the surface treatment time required to form the SAM is relatively long, in the range of several hours. SAM treatment in a short time is important for a high tact-time and production yield in industrial applications. The fundamental properties of OPDs by introducing a SAM on an anode have not been properly investigated under reverse voltage. The present study aims to improve the performance of OPDs by introducing a SAM on an indium–tin-oxide (ITO) electrode under reverse voltage.

In this study, we investigated the improved properties of polymer photodetectors with ITO electrodes modified by phosphonic acid-based SAM formed in a short time. We also focused on the key factors of high sensitivity, color sensitivity, fast response, and high on/off ratio.

## 2. Experimental procedure

Conjugated polymers, P3HT, with various molecular weights ( $M_w = 50$  k, 94 k, 193 k) purchased from Merck KGaA were used as the donor material without further purification. A fluorene-type conjugated polymer, poly(9,9-dioctylfluorene) (F8,  $M_w = 86$  k, ADS129BE), and poly[(9,9-dioctylfluorenyl)-2,7-diyl]-co-( $N,N'$ -diphenyl)- $N,N'$ -di(*p*-butylphenyl)-1,4-diamino-benzene] (PFB  $M_w = 103$  k, ADS232GE) purchased from American Dye Source Inc. were used as the host material without further purification. The fluorene copolymer of poly(9,9-dioctylfluorene-co-bithiophene) (F8T2,  $M_w = 295$  k) was supplied by Sumitomo Chemical Co., Ltd. A fullerene derivative, PCBM, was purchased from Frontier Carbon Inc.

OPDs were fabricated on ITO-coated glass substrates. The glass substrate was degreased with solvents and cleaned in a UV ozone chamber. The SAM treatment procedure in short time is described below. A 2-propanol solution including the SAM first covered the whole set for a minute before being spin-coated on the ITO-coated glass substrate. The solution was spun off at 4000 rpm for 60 s. This step was then followed by thorough rinsing with 2-propanol and then drying. The phosphonic acid-based SAMs, octylphosphonic acid (OPA), and 1H,1H,2H,2H-Perfluorooctanephosphonic acid (FOPA) [26,27] purchased from Sigma–Aldrich Co. were used as typical SAMs. The organic layer was fabricated by spin-coating onto an ITO-coated glass substrate and annealed. The active layer of the OPD was a blend of a donor, F8T2,

and an acceptor, fullerene derivative PCBM, both dissolved in dichlorobenzene with a weight ratio of 1:1. An Al (10 nm)/Ag (100 nm) or MoOx (5 nm)/Au (10 nm)/Ag (100 nm) electrode was vacuum-deposited. The typical active area of the device was 0.3 mm<sup>2</sup>.

Current density–voltage and incident-photon-to-current conversion efficiency (IPCE) characteristics were measured under dark and DC light irradiation from a Xe lamp through the ITO electrode side. Frequency response of the OPD was measured by a fast storage digital oscilloscope (Tektronix TDS 3054) at a bandwidth of 500 MHz. Sinusoidally modulated blue laser diode (LD) ( $\lambda = 408$  nm, 0.57 W/cm<sup>2</sup>) was used as the light source using a driver (Neorark, DSP-5004), and a pulse generator (Agilent 3325A) was used as the voltage source. For measurement of the linear dynamic range, a blue light-emitting diode ( $\lambda = 467$  nm) was used as the light source. Impedance spectroscopy measurements were carried out using a Solatron 1260 impedance analyzer with a 1296 dielectric interface. The typical AC oscillation amplitude was 100 mV. The energy levels of the highest occupied molecular orbitals (HOMOs) of the conjugated polymers and the work function of the ITO electrode were measured by a photoelectron spectrometer (Riken Keiki, AC-2). The bandgap energy was estimated from the edge of the absorption spectrum.

## 3. Results and discussion

Device performance is influenced by chemical and/or physical defects, and the energy barrier at the ITO/organic layer interface. Contact between the anode and the organic layer is one of the key issues in the development of organic devices. The effect of the SAM was characterized in terms of surface free energy and work function of ITO. The surface free energy was estimated from contact angle measurements using distilled water (H<sub>2</sub>O), ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>), and diiodomethane (CH<sub>2</sub>I<sub>2</sub>). To calculate the surface free energy, we employed a solid–liquid adhesion ( $W$ ) equation based on Owen's theory [30], as follows:

$$W = \gamma_{LV}(1 + \cos \theta) = 2(\gamma_s^d \gamma_{LV}^d)^{1/2} + 2(\gamma_s^p \gamma_{LV}^p)^{1/2}, \quad (1)$$

where the superscript  $d$  refers to the dispersion (non-polar) component, and  $p$  refers to the polar (non-dispersion) component including all interactions established between the solid and liquid, such as dipole–dipole, dipole–induced dipole, and hydrogen bonding.  $\gamma_s$  and  $\gamma_{LV}$  refer to the solid and liquid surface free energies, respectively. For ITO without the SAM,  $\gamma_s^d$  and  $\gamma_s^p$  were estimated to be 32.7 and 28.6 mJ/m<sup>2</sup>, respectively. ITO electrodes with FOPA and OPA also had both dispersion and polar components, as shown in Table 1.  $\gamma_s^d$  and  $\gamma_s^p$  of ITO with FOPA (OPA) were estimated to be 12.6 (26.5) and 8.6 (13.1) mJ/m<sup>2</sup>, respectively. ITO electrodes with FOPA and OPA had lower surface free energy compared to those without a SAM and exhibited hydrophobic surfaces, and the surface free energy of an ITO with FOPA (21.2 mJ/m<sup>2</sup>) consisting of fluoroalkyl groups was lower than that with OPA (39.6 mJ/m<sup>2</sup>). Treatment of phosphonic acid-based SAMs, FOPA, and OPA in short time can be applied to modify the surface free energy on ITO. Work functions of ITO

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