



Raman characterization and electrical properties of poly(3-hexylthiophene) doped electrochemically in an ionic liquid-gated transistor geometry



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ABSTRACT

Using Raman spectroscopy, we observed carriers, polarons and bipolarons formed in an ionic-liquid-gated P3HT electrochemical transistor with an ionic liquid [BMIM][TFSI] as a gate dielectric. The relationships between the source–drain current (I_D), the gate voltage (V_G) at a constant source–drain voltage (V_D), and injected charges at each V_G were investigated. An increase in I_D is attributed to the formation of positive polarons, whereas a decrease in I_D corresponded to positive bipolarons. Thus, positive polarons are efficient carriers in P3HT electrochemical transistors. Charge densities, doping levels, electrical conductivities, and mobilities of polarons in P3HT were calculated from the electrochemical measurements. Only positive polarons exist below the dopant level $x = 27$ mol%, whereas at higher doping levels, polarons and bipolarons coexist. The mobility of polarons was dependent on the doping level. The highest mobility was $0.31 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $x = 15$ mol%.

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1. Introduction

Organic thin-film transistors (OTFTs) have attracted considerable interest because of their potential applications in flexible and large-area devices. A polymer electrolyte film, an ion gel or an ionic liquid can function as an ultra-high capacitance gate dielectric in an electrochemical OTFT. The benefits of high capacitance are (1) a high output current at a given applied gating voltage V_G and (2) a low operating V_G . These favorable features originate from the high charge density induced by the high capacitance in the transistor channel.

In an ionic liquid-gated transistor fabricated with regioregular poly(3-hexylthiophene) (P3HT, Fig. 1a) and an ionic liquid as a semiconductor and a gate dielectric, respectively, a negative bias on the gate electrode can lead to the electrochemical doping (oxidation) of the P3HT film between the source and drain electrodes. The charge density (doping level) can be tuned over a wide range by modifying the V_G . The use of an ionic liquid as the gate dielectric can induce a large charge density above 10^{20} cm^{-3} for P3HT [1,2]. At such high charge densities, macroscopic metallic electrical

conductivity is expected [2,3]. When the source–drain voltage V_D is constant, the source–drain current I_D reflects the conductivity of the P3HT film. Paulsen and Frisbie [1] reported that the I_D – V_G curve for such a device exhibited a peak, indicating that as the charge density increased, the conductivity of the P3HT initially increased and then decreased. The decrease in conductivity is undesirable for the transistor. Similar unexpected results have been reported for several types of electrochemical transistors fabricated using certain organic semiconductors [4–13]. The explanations for this phenomenon include band filling [4,8,10] or bipolaron formation [7,9,12,14] at high carrier densities. However, the nature of the charge carriers has not yet been fully elucidated.

Polarons and bipolarons have been proposed as carriers in a conjugated polymer with a non-degenerate ground state [15]. When an electron is removed from a polymer chain, the positive charge $+e$ is localized over several repeating units, leading to structural changes in this region. Such a charge carrier is known as a positive polaron and has a charge of $+e$ and a spin of one-half. When an electron is subsequently removed from a positive polaron, a positive bipolaron is formed with a charge of $+2e$ and no spin. The bipolaron is a spinless carrier. The charge is localized over several repeating units. When a positive polaron or bipolaron is formed, localized electronic levels are formed in the bandgap of the

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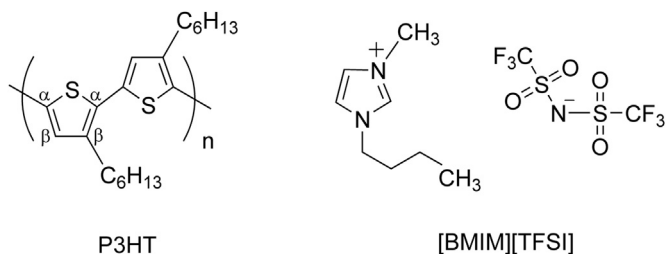


Fig. 1. Chemical structures of P3HT and [BMIM][TFSI].

polymer. Electronic transitions associated with positive polarons and bipolarons appear below the band edge of the polymer in the visible and near-infrared regions [15,16]. The performance of the ionic liquid-gated transistor is associated with carriers, polarons or bipolarons generated in the polymer film of the transistor.

Infrared and Raman spectroscopy provide information about the molecular structures of conjugated and conducting polymers [17,18]. A polaron or a bipolaron can be identified via infrared and Raman spectroscopy [16] because the structural changes associated with the formation of a polaron are different from those of a bipolaron. In particular, *in situ* Raman measurements are very useful for studying carriers generated in the polymer films used in organic transistors. Polarons and bipolarons have been identified for poly(p-phenylenevinylene) [19,20], poly(p-phenylene) [21], and polythiophene [22]. The Raman spectra of doped regioregular poly(3-alkylthiophenes) have been reported [23]. McCreery and colleagues [24,25] conducted Raman studies of electrochemical P3HT memories and observed polarons in the oxidized states of the memories. In a previous work, we reported the Raman spectra of polarons and bipolarons formed by chemical doping [26]. According to a theoretical study by Shimoi and Abe [27], polarons are formed at low doping levels, whereas bipolarons are formed at high doping levels; thus, there exists a critical doping level. However, the critical doping level has not been experimentally determined.

In this article, we present a Raman spectroscopy study of carriers generated in a P3HT film used for an ionic liquid-gated transistor. The ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([BMIM][TFSI]) (Fig. 1b) was used as the electrolyte (gate dielectric) in the transistor. The dependence of the Raman spectra on the V_G was measured and attributed to positive polarons and bipolarons. The dependence of the current (I_D) on the V_G between the source and drain electrodes for the transistor was measured and discussed in terms of the polarons and bipolarons in the P3HT. The charge density, doping level, electrical conductivity, and mobility of the polarons in the P3HT film were obtained from electrochemical measurements.

2. Experimental methods

2.1. Materials and devices

Regioregular P3HT and [BMIM][TFSI] were purchased from Sigma-Aldrich and used as received. Acetonitrile, anhydrous iron (III) chloride, and chlorobenzene were purchased from Kanto Kagaku. A glass substrate coated with indium-tin oxide (ITO) was purchased from Itoh Optical Industrial. The sheet resistivity of the ITO-coated glass substrate was $41 \Omega \text{ sq}^{-1}$.

The electrochemical transistor used in this work is depicted in Fig. 2. The source and drain electrodes were formed by vacuum deposition method using a shadow mask. A 5 nm adhesion layer of Ni was deposited followed by 50 nm of Au on a glass substrate. A P3HT film was prepared from a chlorobenzene solution of P3HT

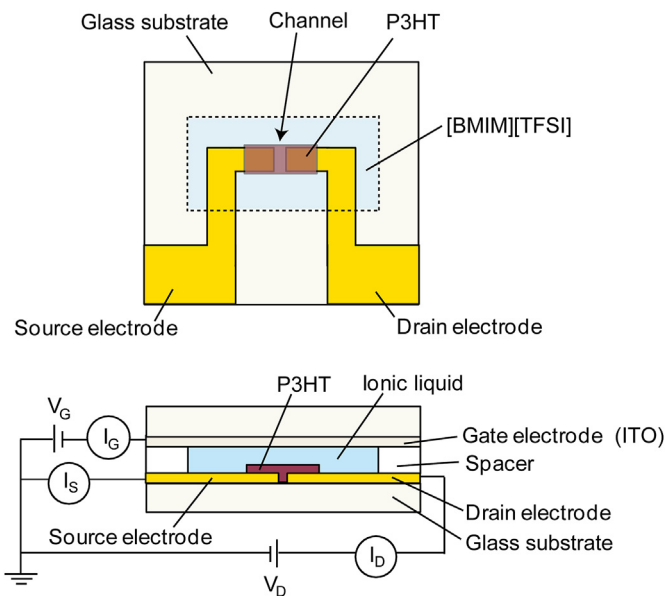


Fig. 2. Configuration of the ionic liquid-gated transistor fabricated with P3HT and [BMIM][TFSI].

(24 mg mL⁻¹) using the spin-coating method. The film was not annealed. The thickness of the P3HT film was 1.0×10^2 nm. The width and the length of the channel of the transistor were $6.0 \times 10^2 \mu\text{m}$ and $7.14 \times 10 \mu\text{m}$, respectively. The ionic liquid [BMIM][TFSI] was used as the electrolyte. An ITO-coated glass substrate was used as the gate electrode. The thickness of the [BMIM][TFSI] layer was set to $1.25 \times 10^2 \mu\text{m}$ using a polyethylene terephthalate spacer.

A diode-type electrochemical cell fabricated for visible/near-infrared (Vis/NIR) absorption measurements is depicted in Fig. 3. A thin film of P3HT was formed on the surface of an ITO-coated glass substrate via spin-coating using a chlorobenzene solution of P3HT (24 mg mL⁻¹) and was subsequently used as the working electrode. The thickness of the P3HT layer was 1.0×10^2 nm. An ITO-coated glass substrate was used as the counter electrode. The ionic liquid [BMIM][TFSI] was sandwiched between the working and counter electrodes. The separation between the two electrodes was set to $1.50 \times 10^2 \mu\text{m}$ using a Teflon spacer.

A P3HT film was chemically oxidized by immersion in an acetonitrile solution of anhydrous FeCl₃ (0.01 mol L⁻¹) for 5 min. Another P3HT film was also chemically oxidized by exposure to FeCl₃ vapor at a reduced pressure for 20 h.

2.2. Electrochemical measurements

The injected charge density n (cm⁻³) at each V_G value was obtained using a method similar to that of Harada et al. [3]. The time

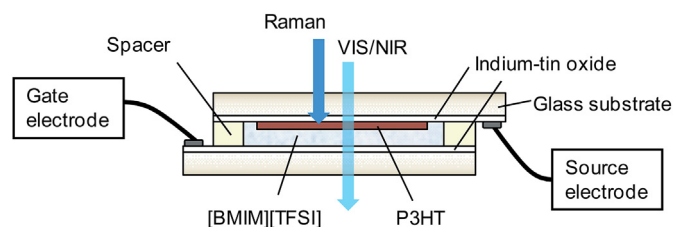


Fig. 3. Configuration of the MIS diode fabricated with P3HT and [BMIM][TFSI] for spectroscopic measurements.

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