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A Relationship between Molecular Orientation and Current–Voltage Characteristics in Poly(3-hexylthiophene) Thin Film

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Simultaneous measurement of molecular orientation and current as a function of voltage has been conducted. Molecular orientation was measured using the polarization dependence of intramolecular electronic transition. In ITO/poly(3-hexylthiophene)/Al structure, it was found that the molecular orientation change assists the hysteretic current–voltage (*J*–*V*) characteristics. The result indicates that this measuring method can be useful in investigating the effects of molecular orientation change on unusual *J*–*V* characteristics.

Molecular switching devices have been extensively studied because of their potential use in logic circuits and memory devices. In these studies, many mechanisms of unusual current–voltage (*J*–*V*) characteristics, including switching and hysteretic behavior, have been proposed. A redox reaction[1–3] and a change in a molecular conformation[2–5] or orientation[6] are some examples of the reported mechanisms. However, there have been few reports of direct evidence suggesting relationships between *J*–*V* characteristics and proposed mechanisms, as it is difficult to conduct simultaneous measurements of *J*–*V* characteristics and other parameters to confirm the origin of the mechanism. In fact, most of the mechanisms have been investigated by quantum mechanical calculation and/or measurement of (tunneling) current as a function of voltage. However, a relationship between molecular orientation and *J*–*V* characteristics can directly be investigated because molecular orientation can be proved by the polarization dependence of intramolecular electronic transition (polarized absorption),[7,8] which can simultaneously be measured with *J*–*V* characteristics. Thus, we have attempted to conduct a simultaneous measurement of molecular orientation and *J*–*V* characteristics. As the first step, we have chosen poly(3-hexylthiophene) (P3HT; Figure 1) thin film as the target because P3HT has been reported as the material having a correlation between the orientation state and the electric conduction.[9,10]

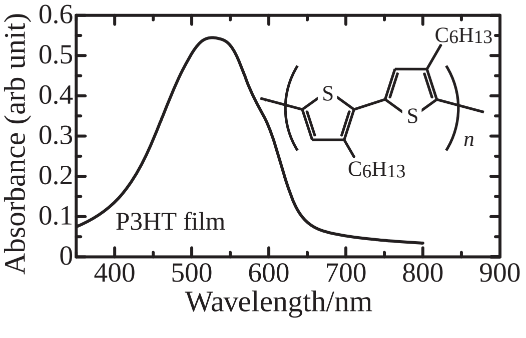

Figure 1. The absorption spectra of P3HT film. The absorption band of the π–π^* transition of P3HT appeared in the visible region.

The regioregular P3HT was purchased from Aldrich and used without further purification. A thin film of P3HT was fabricated from a chloroform solution (1 mg/mL) on the ITO electrode by a spin-coating technique; the film thickness was 100 nm. After the film fabrication, Al was deposited on the film by vacuum deposition.

A *J*–*V* characteristics was measured by applying a positive and negative voltage to an ITO and an Al electrodes, respectively. Simultaneously, in order to prove an orientation state, the polarized absorption was measured at incident angle (θ) of 45°. The experimental setup is shown in Figure 2. The exciting lights were s- and p-polarized lights from light-emitting diodes (LEDs) with polarizers. Here, the s- and p-polarization are defined as perpendicular and parallel to the plane of incidence, respectively. The exciting wavelength was 550 nm corresponding to π–π^* transition energy of P3HT conjugated backbone (Figure 1).[11] The sample was illuminated by the s- and p-polarized lights from LEDs, which were driven with rectangular voltage pulses (900 Hz, 50% duty ratio). The phase difference between the s- and p-polarized lights was set to 180°. Then, the polarized lights were passed through the sample and detected by a photomultiplier tube connected to a lock-in amplifier and a DC voltmeter through a preamplifier. The difference in intensities ($\Delta I = I_\mathrm{p} - I_\mathrm{s}$) was measured by the lock-in amplifier, while the total ($I = I_\mathrm{p} + I_\mathrm{s}$) was measured by a DC voltmeter. Herein, I_p and I_s are the intensities of p- and s-polarized transmitted lights, respectively. Before the measurement, ΔI was tuned to zero as initializing ($I_\mathrm{p} = I_\mathrm{s} = I_0/2$ in initial state). All the measurements were conducted in air.

From ΔI and I measurements, we can obtain $\Delta I/I$ and $1 - I/I_0$ given by eqs 1–4.[12] Herein, β, d, and α are the absorption coefficient, film thickness, and the angle between normal of a substrate and average of the transition dipoles ($\boldsymbol{\mu}$) (Figure 3). Note that $\Delta\alpha$ gives the change of molecular orientation, and

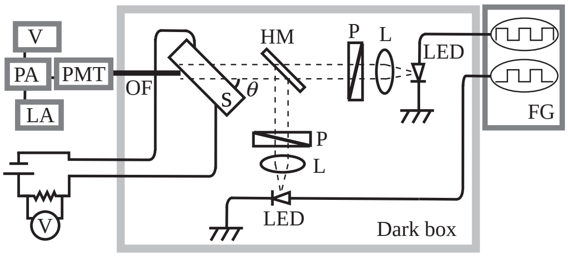

Figure 2. Experimental setup for molecular orientation and current–voltage measurement. V, voltmeter; PA, preamplifier; LA, lock-in amplifier; PMT, photomultiplier tube; OF, optical fiber; S, sample film; HM, half mirror; P, polarizer; L, lens; LED, light-emitting diode; FG, function generator. θ is the angle between the sample surface and incident beam. Broken lines represent light beams.

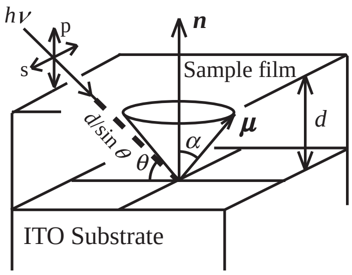

Figure 3. Schematic model for molecular orientation in a thin film on an ITO substrate. p, s, polarized direction; **n**, normal of ITO substrate; d, film thickness; $\boldsymbol{\mu}$, average of transition dipoles of the whole P3HT molecules on the incident beam; α, angle between **n** and $\boldsymbol{\mu}$; θ, angle between the sample surface and incident beam. The broken line represents optical length in a thin film.

$\Delta(\beta d)$ represents a spectral change not associated with molecular orientation change (for example, Stark effect).

$$\frac{\Delta I}{I} = 3\cos^2\theta\left(\frac{\beta d\sin\alpha\cos\alpha}{2\sin\theta}\right)\Delta\alpha + (A - B)\Delta(\beta d) \quad (1)$$

$$1 - \frac{I}{I_0} = (2\sin^2\theta - \cos^2\theta)\left(\frac{\beta d\sin\alpha\cos\alpha}{2\sin\theta}\right)\Delta\alpha + (A + B)\Delta(\beta d) \quad (2)$$

$$A = \frac{\sin^2\alpha}{4\sin\theta} \quad (3)$$

$$B = \frac{2\cos^2\theta\cos^2\alpha + \sin^2\theta\sin^2\alpha}{4\sin\theta} \quad (4)$$

Equations 1–4 demonstrate that $\Delta\alpha$ and $\Delta(\beta d)$ are possible to cause the change of $\Delta I/I$ and $1 - I/I_0$. From the ratio $(1 - I/I_0)/(\Delta I/I)$, however, we can clarify which contribution is dominant. The ratio is given by $(2\sin^2\theta - \cos^2\theta)/(3\cos^2\theta)$ $(= 1/3$ at $\theta = 45°)$ when $\Delta(\beta d) = 0$. On the other hand, it is $(A + B)/(A - B) > 1$ when $\Delta\alpha = 0$.

Figure 4a shows the J–V characteristics. Hysteretic loop appeared in the J–V characteristics. Each loop is traversed as indicated by arrows and can be cycled repeatedly. Similarly, as shown in Figures 4b and 4c, hysteretic loops appeared also in the $\Delta I/I$–V and the $(1 - I/I_0)$–V characteristics. The ratio $(1 - I/I_0)/(\Delta I/I)$ is approximately 0.2. This corresponds to $\theta = 42°$. This value is roughly consistent with the incident angle of $\theta = 45°$.[13] This indicates that $\Delta(\beta d)$ is negligible in the present case, and the changes of $\Delta I/I$ and $1 - I/I_0$ are caused by the molecular orientation change.

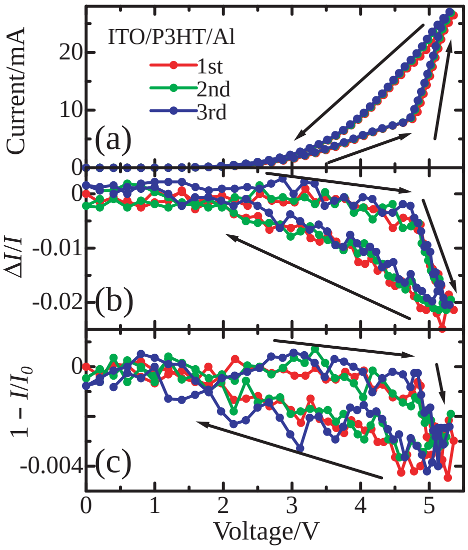

Figure 4. (a) The J–V, (b) $\Delta I/I$–V and (c) $(1 - I/I_0)$–V characteristics. The pointing arrows represent a sequence of the voltage sweep.

Because the eq 1 indicates that $\Delta I/I$ is proportional to $\Delta\alpha$, the result shown in Figure 4b suggests that the main chain of P3HT tends upright (or lying) on the substrate when we increase (or decrease) the bias voltage. Using experimentally obtained values[8] of βd and α ($\beta d \approx 0.5$; $\alpha \approx 75°$), $\Delta\alpha$ is evaluated to be ca. 0.2°. Since the molecular orientation affects the electric characteristics,[9,10] we speculate that the hysteretic J–V characteristics was caused by the molecular orientation change. Although the detailed mechanism is not clear at the present stage, this orientation change may be associated with the increase of electric field or joule heating.

In conclusion, the simultaneous measurement of current, $\Delta I/I$ and $1 - I/I_0$ as a function of voltage is of use for direct investigation of the relationship between molecular orientation and unusual electric characteristics, which have been much reported recently. By applying the method to ITO/P3HT/Al junction, we could clarify that the orientation change of the P3HT chain causes the reproducible loop of the J–V characteristics.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
13 Since film thichness is much less than the wavelength, Snell's law does not hold in the present case.

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