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Infrared Spectroscopy of Electroluminescent Conjugated Polymers

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Summary: The infrared spectra of the light-emitting diodes and the metal-insulator-semiconductor devices based on a poly(p-phenylenevinylene) derivative MEH-PPV have been measured *in situ* with a reflection configuration. The voltage-induced infrared spectra of these devices have been measured by the FT-IR difference-spectrum method. The observed bands have been attributed to the carriers injected into the polymer layers. The observation of positive carriers in the polymer light-emitting diode is probably related to the predominance of injected positive carriers, which is one of the factors in the low efficiency of the polymer light-emitting diode. *In situ* infrared reflective absorption measurements provide the information about injected carriers, which play a central role in the properties and the functions of polymer electronic devices.

Introduction

Organic materials including conjugated polymers have been incorporated as the active semiconductors in electronic devices such as light-emitting diodes (LEDs) and displays.[1,2] Polymer LEDs have the potential to provide an innovative low-cost technology for illumination and display applications through a simple coating procedure. Poly(*p*-phenylenevinylene) (PPV) derivatives and polyfluorene derivatives are promising materials for light-emitting devices. In a single-layer light-emitting diode, a thin layer of a polymer is sandwiched by an indium-tin oxide (ITO) electrode (anode) and a metal electrode

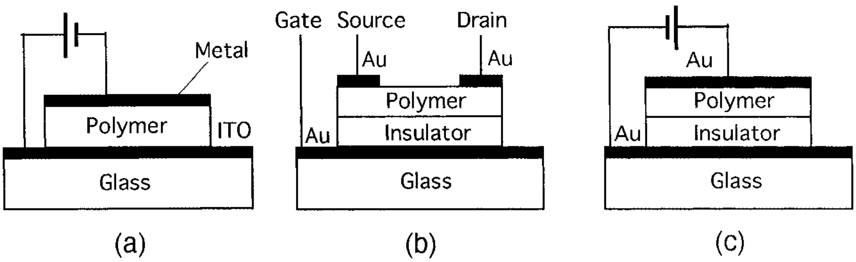

Figure 1. Schematic polymer electronic devices: (a) single-layer light emitting diode; (b) field-effect transistor; (c) metal-insulator-semiconductor diode.

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(cathode), as shown in Fig 1a. When a forward bias is applied between these electrodes, light emission occurs. This is called electroluminescence. Recently, Batlogg and coworkers have reported superconductivity transitions in hole-doped C_{60} single crystals at 52 K[3] and in the solution-cast films of regioregular poly(3-hexylthiophene) at 2.35 K[4] by using the field-effect-device geometry. A field-effect transistor (FET) has three electrodes called source, drain, and gate, as shown in Fig. 1b. In this device, carriers are induced by the application of a voltage between the gate and the source-drain electrodes. This is called field-effect doping. The field-effect-doping technique has opened a new field of superconductivity in organic materials. A metal-insulator-semiconductor (MIS) diode shown in Fig. 1c is a central part of the field-effect transistor. The studies on MIS diodes can lead us to the understanding of the field-effect transistors. In the organic devices, there are several problems to be solved: the structures and the orientations of organic compounds; the interactions between organic compounds and metal electrodes; carrier injection; the formation and the recombination of excitons. Infrared spectroscopy is expected to give us information about these problems. In particular, the properties and the functions of organic electronic devices are strongly associated with the charge carriers generated in organic materials. We have demonstrated that *in situ* infrared reflective absorption measurements are useful for investigating polymer LEDs.[5,6] In this work, we present the results of infrared studies on the single-layer light-emitting diodes and the MIS diodes fabricated with poly(*p*-phenylenevinylene) (PPV) derivatives (see Fig. 2).

Device Preparation

Single-layer LEDs were made according to a previous paper.[7] Barium fluoride (BaF_2) plates coated with indium-tin oxide (ITO) were used as the substrates of LEDs. The thickness of the ITO layer was about 8 nm. The transmission of these plates in the mid-

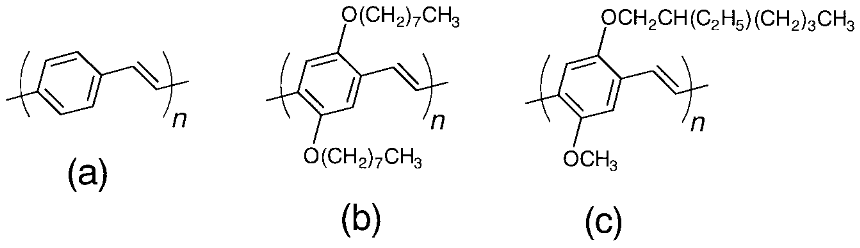

Figure 2. Chemical structures of (a) poly(*p*-phenylenevinylene) (PPV), (b) poly(2,5-dioctyloxy-*p*-phenylenevinylene) (DOO-PPV), and (c) poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV).

infrared region was about 80%. A thin film of a PPV derivative was formed on the ITO-coated BaF_2 plate by the spin-coating technique. The thickness of the polymer layer was about 100 nm. Aluminum-lithium alloy was evaporated onto the polymer layer, and aluminum was overcoated for the protection of the Al-Li alloy. The ITO and Al-Li electrodes were used as anode and cathode, respectively. The active area of the diodes was 6 mm^2.

MIS diodes were made as follows. Gold was thermally evaporated onto a glass substrate and used as the gate electrode. Aluminum oxide was then sputtered onto this gold layer. The thickness of the aluminum oxide layer was about 250 nm. A film of a PPV derivative was formed on the aluminum oxide layer. A film of gold (thickness, 12 nm) was formed on the polymer layer by heat evaporation.

Infrared Measurements

The infrared spectra of the polymer electronic devices were recorded with a Bio-Rad FTS 175 FT-IR spectrophotometer by using a single attenuated total reflection (ATR) accessory (Golden Gate^{TM}). The plate equipped with an ATR prism was replaced by a home-made plate as the sample stage of an organic electronic device. The incident angle of this accessory was fixed to be 45 degree. Infrared light was incident on the BaF_2 substrate of a polymer LED. The incident light passed through the ITO and polymer layers, and then reflected by the metal electrode. The reflected light passed through the polymer and ITO layers and the BaF_2 substrate. The infrared spectrum obtained from the metal electrode with no contribution of the polymer layer was used for the reference spectrum in calculating absorbance spectra. In the case of an MIS diode, infrared light was incident on the overcoated thin Au layer. A thin film of gold can transmit infrared light. The transmitted light passed through the polymer layer and reflected by the Au gate electrode. The reflected light passed through the polymer layer again. Voltage-induced infrared spectra were measured by using the FT-IR difference-spectrum method.

Results and Discussion

The infrared spectra of an LED fabricated with MEH-PPV (Fig. 2c) with the P and S polarizations are shown in Fig. 3. All of the observed bands are attributable to MEH-PPV. Since the thickness of the MEH-PPV layer is about 100 nm, infrared absorption spectra are obtained by using the reflection configuration. Thus, these spectra are called reflective

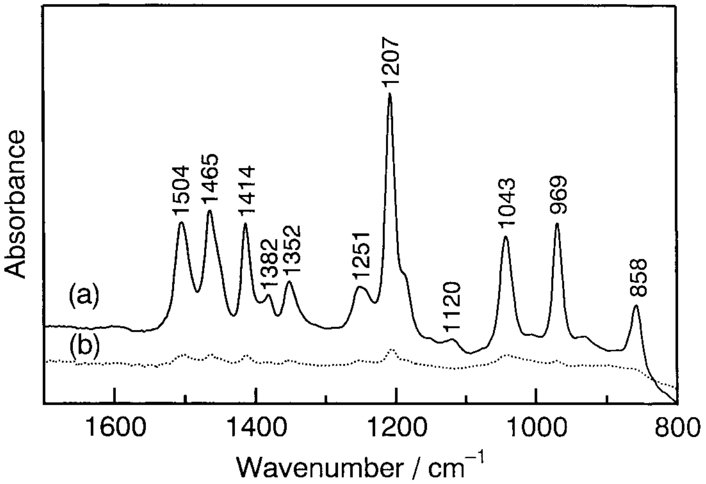

Figure 3. Infrared reflective absorption spectra of an MEH-PPV LED: (a) P polarization; (b) S polarization.

absorption spectra. The intensities of the bands with the S polarization are very weak. This is because the electric field of the incident light is almost cancelled out by that of the reflected light at the metal surface, as the case of infrared reflection-absorption measurements.[8] The thickness of the polymer layer is about 100 nm. It is safe to consider that the value of 100 nm is much smaller than that of the wavelength of infrared light; for example, the wavelength of infrared light at 2000 cm^{-1} is 5 μm. It is necessary for us to take this surface effect into account for the orientation analyses of the polymers in LEDs.

The voltage-induced infrared spectrum of the LED fabricated with MEH-PPV is shown in Fig. 4a. The observed spectrum is quite different from that of MEH-PPV. The observed bands are attributable to the carriers injected into the MEH-PPV layer. The infrared absorption induced by iodine (acceptor) doping is shown in Fig. 4b. Upon iodine doping, positive carriers and anions such as $(I_3^-)_x$ are formed. The infrared absorption induced by Na (donor) doping is shown in Fig. 4c. Upon Na doping, negative carriers and cations (Na^+) are formed. The carriers in conjugated polymers such as MEH-PPV are not merely electrons or holes, but charged quasi-particles with structural changes extending over several repeating units.[9] They can move on a polymer chain with structural changes and hop from a chain to the neighboring one. They show characteristic infrared-active

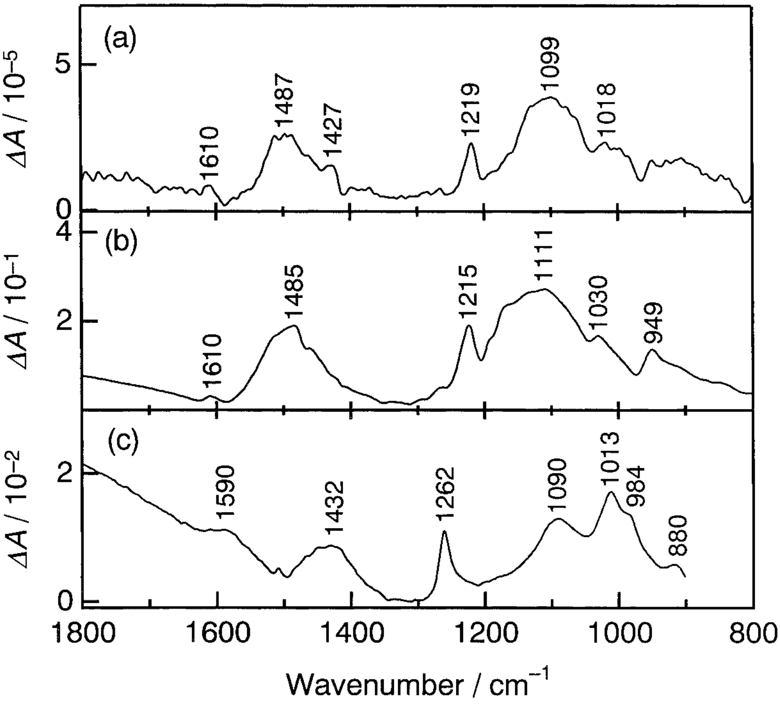

Figure 4. (a) Voltage-induced, (b) iodine-doping-induced, and (c) Na-doping-induced infrared spectra of MEH-PPV.

vibrations (IRAVs), because they are associated with structural changes.[10] The IRAVs associated with positive and negative carriers are observed in Figs. 4b and 4c, respectively. The voltage-induced infrared spectrum is similar to iodine-doping-induced one. Thus, positive carriers are mainly observed in the voltage-induced spectrum.

The infrared result can be related to the efficiency of polymer LEDs, as discussed below. The efficiency of polymer LEDs η_{int} can be expressed by

$$\eta_{\mathrm{int}} = \gamma \eta_{\mathrm{st}} \phi \qquad (1)$$

where γ is the ratio of the number of exciton formation events within the LED to the number of electrons flowing in the internal circuit; η_{st} is the fraction of the formation of singlet excitons; ϕ is the quantum efficiency of the radiative decay of singlet excitons.[2]

Since the electroluminescence in polymer LEDs originates from singlet excitons, the value of η_{st} is about 0.25, according to spin statistics.[11] The γ is the most important factor determining the efficiency of LEDs. It should be noted that the number of injected negative carriers is not necessarily the same as that of injected positive carriers. The γ value depends on the ratio of injected positive and negative carriers. When the number of injected positive carriers is the same as that of injected negative carriers, the value of γ is equal to unity. In general, the γ values of polymer LEDs are less than unity. On the basis of the consideration described above, the result of the voltage-induced infrared measurements suggests that injected carriers are unbalanced in the MEH-PPV LED. The voltage-induced infrared spectrum from the LED fabricated with DOO-PPV (Fig. 2b) has been also attributed to injected positive carriers.[5] The efficiency of the DOO-PPV LED is also low. Probably the infrared results are related to the unbalance of injected carriers.

The capacitance *versus* voltage (*CV*) plots are useful for checking that the MIS device is charging properly. The *CV* plot of the MIS diode fabricated with MEH-PPV is shown in Fig. 5. The observed curve is similar to that of the MIS diode fabricated with regioregular poly(3-hexylthiophene).[12] When a negative bias is applied to the gate electrode with respect to the other Au electrode, positive carriers are accumulated at the polymer-insulator interface. In the negative bias region of the *CV* curve, capacitance shows a plateau at a

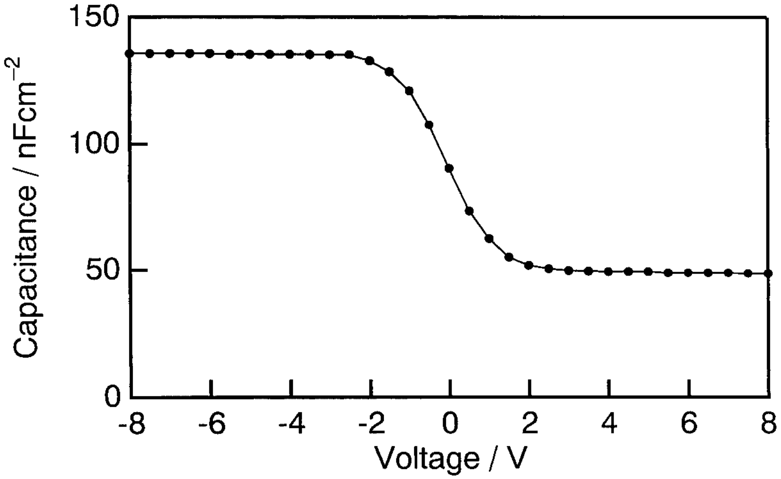

Figure 5. CV plot of an MIS diode fabricated with MEH-PPV measured at 1 kHz.

high value of 136 nFcm^{-2}. In this region, we can measure the capacitance of the aluminum oxide layer only; it depends on the dielectric constant, the thickness, and the active area of the aluminum oxide layer. It is considered that charge is generated at the thin region of the MEH-PPV layer at the polymer-insulator interface.[3,4] The induced charge density under the voltage $-V$ is equal to CV/eA, where A is the active area of the diode, and e is elementary electric charge. The charge density at –3 V is calculated to be 2.6×10^{12} cm^{-2}. In the positive bias region, capacitance shows a plateau at a low value. In this region, carriers are not accumulated. The infrared difference spectrum of the MEH-PPV MIS diode between –3 V and +3 V is shown in Fig. 6. The observed voltage-induced infrared spectrum is attributed to the carriers accumulated in the MEH-PPV layer. We have succeeded in observing the infrared bands due to the carriers induced by field-effect doping.

Conclusions

It has been demonstrated that *in situ* infrared reflective absorption spectroscopy is useful for studying polymer light-emitting diodes and metal-insulator-semiconductor diodes. The infrared absorptions due to the carriers injected into the polymer layers have been obtained

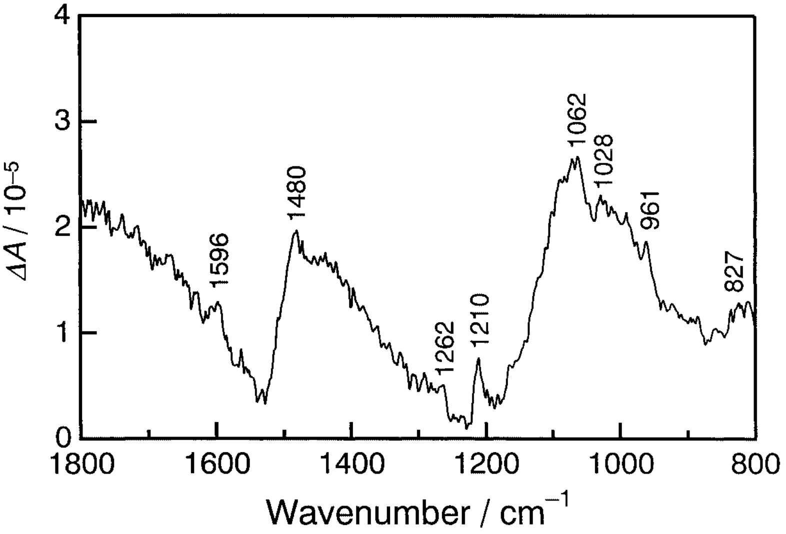

Figure 6. Voltage-induced infrared reflective absorption spectrum of an MIS diode fabricated with MEH-PPV.

by the FT-IR difference-spectrum method. The infrared results give us the information about the charge balance, which determines the efficiencies of polymer light-emitting diodes. The infrared bands due to the carriers generated by field-effect doping have been obtained.

Acknowledgments

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[1] S. Miyata and H. S. Nalwa Eds., "*Organic Electroluminescent Materials and Devices*", Gordon and Breach, Amsterdam, 1997.
[2] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.
[3] J. H. Schön, Ch. Kloc, B. Batlogg, *Nature* **2000**, *408*, 549.
[4] J. H. Schön, A. Dodabalapur, Z. Bao, Ch. Kloc, O. Schenker, B. Batlogg, *Nature* **2001**, *410*, 189.
[5] M. Ishima, Y. Furukawa, T. Noguchi, T. Ohnishi, Proceedings of the Twelfth International Conference on Fourier-Transform Spectroscopy, Waseda University Press, 2000, p. 423.
[6] Y. Furukawa, M. Ishima, T. Noguchi, T. Ohnishi, *Synth. Met.* **2001**, *121*, 1649.
[7] S. Doi, M. Kuwabara, T. Noguchi, T. Ohnishi, *Synth. Met.* **1993**, *57*, 4174.
[8] R. G. Greenler, *J. Chem. Phys.* **1966**, *44*, 310.
[9] Y. Furukawa, *J. Phys. Chem.* **1996**, *100*, 15644.
[10] M. Gussoni, C. Castiglioni, G. Zerbi, In: "*Spectroscopy of Advanced Materials*", R. J. H. Clark and R. E. Hester, Eds., John, Wiley & Sons, Chichester, 1991, pp. 251–353.
[11] A. R. Brown, K. Pichler, N. C. Greenham, D. D. C. Bradley, R. H. Friend, A. B. Holmes, *Chem. Phys. Lett.* **1993**, *210*, 61.
[12] P. J. Brown, H. Sirringhaus, R. H. Friend, *Synth. Met.* **1999**, *101*, 557.