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Luminescence and photoelectric properties of thiophene dendrimer spin-coated films ☆

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Abstract

Thiophene dendrimer spin-coated films were fabricated and the optical and photoelectric properties were investigated. Absorption edge and peak of photoluminescence (PL) spectra for the film were observed at around 550 and 618 nm, respectively. The excitation spectrum almost corresponded with optical absorption. From the voltage vs. current properties, the Schottky conductions were estimated in the indium tin oxide (ITO)/dendrimer/Al device. Photoelectric properties were also observed and the action spectra of the photocurrent in the device also corresponded with the absorption spectrum.

Keywords: Dendrimer; Thiophene; Spin-coating; Photocurrent; Photoluminescence

1. Introduction

Thiophene oligomers or polymers are quite useful for fabricating various kinds of electric devices, such as organic light emitting diodes, field effect transistors, solar cells and so on [1–5]. Furthermore, thiophenes are very easy to control the optical and electrical properties by doping. However, appropriate substitute groups must be introduced to give solubility and structure control to the system. Recently, dendrimers are attracting much interest because of their unique structure and various noble properties [6]. Especially, dendrimers with conjugated system are quite useful for organic light emitting diodes, sensors and photoelectric systems.

In this study, thin films were fabricated using spin-coating method for newly synthesized thiophene dendrimer [7,8]. The dendrimers are considered to be quite promising for energy transfer system, antenna molecule and so on [9,10]. The optical and fundamental photoelectric properties were investigated for the films.

2. Experimental detail

Fig. 1 shows the thiophene dendrimer used in this study. Toluene containing 2.3 wt% thiophene dendrimer was used for the film fabrication. The solution was dropped on freshly cleaned quartz substrates or glass substrates covered with indium tin oxide (ITO) film. The dendrimer films on the quartz substrates were used for photoluminescence (PL) measurements. For the electrical property measurements, ITO/dendrimer/Al devices were fabricated. The Al films were vacuum evaporated as cathode and the effective electrode area is about 12 mm^2. At the interface between dendrimer and Al film, Schottky contact is expected because the dendrimer indicates p-type conduction. The thicknesses of the dendrimer films were obtained using atomic force

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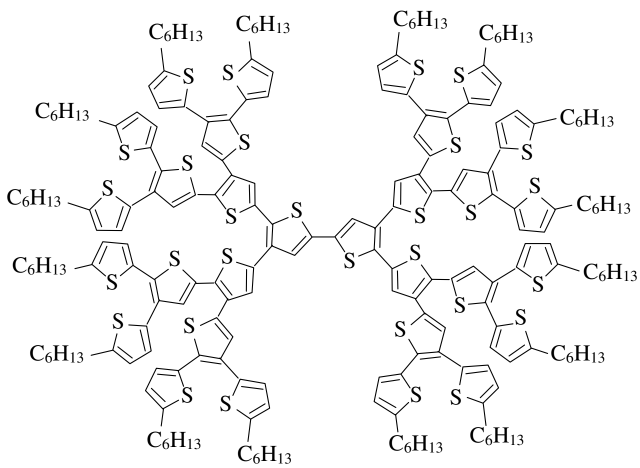

Fig. 1. Structure of the thiophene dendrimer.

microscopy (AFM, Nanoscope IIIa, digital instruments).

The absorption and photoluminescence (PL) properties of the dendrimer solutions and films were observed using multichannel photodetector system (IMUC-7000, Otsuka denshi). A xenon lump and a monochrometer were used for excitation. The absorption and PL spectra of toluene solution were obtained by the same system combined with quartz quvette ($l = 1$ cm).

The voltage vs. current (V–I) properties of ITO/dendrimer/Al device were observed in air and in vacuum of about 1 mTorr using triangular Lissajous method ($f = 0.01$ Hz). The polarity of the voltage was set as forward when the positive voltage was applied to ITO electrode. V–I properties were also observed under white light illumination of 40 mW/cm^2 from the xenon lamp. Action spectra of short-circuit photocurrent (I_{SC}) for the device were also observed using the monochrometer and the xenon lamp.

3. Results and discussion

Fig. 2(a) shows the absorption and PL spectra of the thiophene dendrimer solution in toluene of 0.02 wt% concentration and spin-coated film with 70 nm thickness. The absorption edges of thiophene dendrimer are at around 500 and 550 nm in solution and spin-coated film, respectively. Furthermore, the peaks of PL spectra were observed at 580 nm for solution and 618 nm for film. These differences in absorption and PL spectra are considered to be due to some kind of molecular stacking in the film. The excitation spectrum was also observed in the region from 580 nm to 390 nm and almost corresponded to the absorption spectrum as shown in Fig. 2(b). The shape of PL spectra did not change with the excitation wavelength in the region. Various conjugated length exist in the dendrimer and energy transfer from shorter-conjugated branches to longer one can account for the independence from the excitation wavelength.

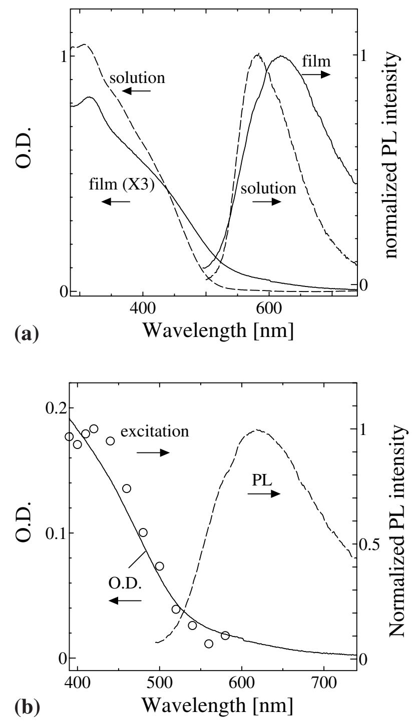

Fig. 2. UV–vis absorption and photoluminescence spectra (a) and excitation spectra of the thiophene dendrimer spin-coated film (b).

Fig. 3(a) shows linear plots of forward bias voltage vs. current properties of ITO/dendrimer (70 nm)/Al device in vacuum and in air. The currents of the device observed in air are larger than those observed in vacuum. It is probably due to adsorbed oxygen molecules which work as dopant in the device. The currents in the device under light illumination are also larger than those in the dark due to photocarrier generation in the device. The open-circuit voltages were about 0.3 V and short-circuit photocurrents were about several nA for the device. The open-circuit voltages and short-circuit photocurrents also depend on the atmosphere, which were considered to be due to adsorption of oxygen.

Relations between square root of voltage vs. logarithm of the current in the device are shown in Fig. 3(b). The plots are linear in large voltage region, which suggests the Schottky or Pool-Frenkel conduction as shown in the next equation,

$$I \approx \exp\left(\beta(\sqrt{E})/kT\right) \tag{1}$$

where E is the electric field, k is the Boltzmann constant and T is temperature. β can be shown in the next equations,

$$\beta_{PF} = (e^3/\varepsilon\pi)^{1/2}$$

in case of the Poole–Frenkel conduction, (2a)

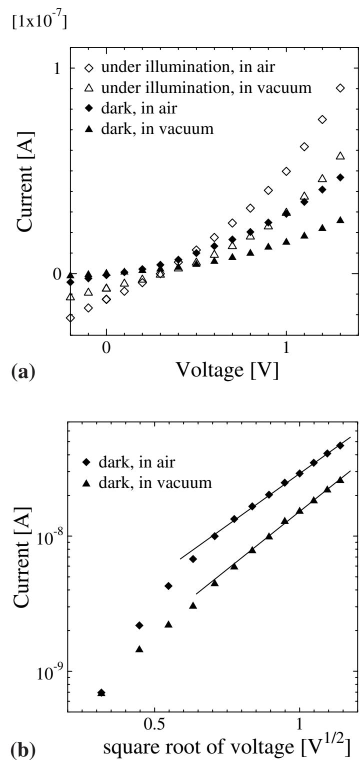

Fig. 3. Voltage vs. current (V–I) properties of ITO/dendrimer/Al device: (a) linearly plotted V–I curve in air and in vacuum with and without light irradiation and (b) relations between the square root of applied voltage and the logarithm of the current in air and in vacuum.

$$\beta_S = (e^3/4\varepsilon\pi)^{1/2} \text{ in case of the Schottky conduction,} \tag{2b}$$

where e is elementary electric charge and ε is dielectric constant.

If we assume relative dielectric constant of the dendrimer is 2.5, theoretical β_{PF} and β_S can be calculated as 7.7×10^{-24} and 3.8×10^{-24}, respectively. Experimental β calculated from the slope of the V–I curve were calculated as 4.0×10^{-24} for the device in vacuum and 3.7×10^{-24} for that in air. The each experimental β is close to the theoretical Schottky one, so it is considered that the currents are dominated by the Schottky conduction.

The short-circuit photocurrents at various wavelength, that is, photocurrent action spectrum was observed for the device. The result is shown in Fig. 4. The currents are normalized as the irradiated light power of 1 μW/cm^2. The action spectra also almost corresponded to absorption spectrum, which means the photocarrier generation due to dendrimer film. The device structure is not optimized, so the photocurrents are not so large. Further experiments are being carried out for performance improvement and for constructing photoelectric devices using the dendrimer.

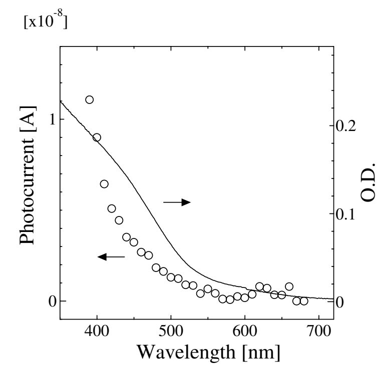

Fig. 4. The short circuit photocurrent property of ITO/dendrimer/Al device.

4. Conclusion

Spin-coated thin films were fabricated using newly synthesized thiophene dendrimer. Photoluminescence spectra with peak at 618 nm were observed in the film and the excitation spectrum almost corresponded with the absorption one. From the voltage vs. current property of ITO/dendrimer/Al device, it was considered that the current was dominated by the Schottky conduction. The photocurrent action spectrum corresponded to the absorption spectrum of the dendrimer film. Further experiments are being performed for fabricating solar cell, light emitting diode and so on.

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