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Optical properties and microring laser of conducting polymers with Sn atoms in main chains

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Optical properties of conducting polymers with Sn atoms in main chains, such as optical absorption, photoluminescence (PL), and electroluminescence, have been studied. The electronic energy structures have been determined by optical and electrochemical measurements. Strong PL with high quantum efficiency has been clarified in the films, and photopumped multimode laser emission was demonstrated from cylindrical microcavities formed by these polymers coated around optical fibers.

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I. INTRODUCTION

The use of π -conjugated conducting polymers as functional materials has attracted much attention from the point of view of basic science and applications, because of their high processability, stability, and promising electrical and optical properties.¹ Among various conducting polymers, alkyl- or alkoxy-substituted polymers, such as poly(3-alkylthiophene),² poly(9,9-dialkylfluorene) (PDAF),^{3,4} poly(*p*-phenylene) (PPP) derivative,⁵ and poly(2,5-dialkoxy-*p*-phenylene vinylene)^{6,7} are the most attractive materials, because of their fusibility at relatively low temperatures, solubility in common solvents, and their high luminescent quantum efficiency.

Utilizing conducting polymers with relatively large bandgap, polymer blue light-emitting diodes (LED)^{8–10} or polymer blue lasers could be realized. We have demonstrated the blue LEDs by utilizing PDAF,³ PPP derivative,⁵ or polyacetylene derivative¹¹ as emission layers. Though red and green photopumped lasers with microcavities of π -conjugated polymers were demonstrated previously, blue region lasers have hardly been reported.

On the other hand, copolymers with a π -conjugated segment and hetero atoms, such as Si and Sn, which are the same group of carbon atom in each monomer unit of polymer main chains, are expected to possess unique characteristics and functionalities. Recently, copolymers such as poly(disilanyleneoligophenylene)s¹² and poly(disilanyleneoligothienylene)s¹³ were synthesized and demonstrated the blue-to-red electroluminescent (EL) properties, since Si in main chains interrupts the π -conjugated chain and limit the π -conjugation length. Furthermore, they were highly soluble in common solvents and the high-quality thin films could be obtained in wet processes, because the long bond length between a hetero atom and a carbon atom reduces its rigidity. Copolymers synthesized by the modified synthetic process

should also have another π -conjugated segment and a possibility to exhibit unique luminescent properties.

In this paper, we report the optical properties, such as photoluminescence (PL), spectral narrowing of PL, the EL properties of conducting polymers with Sn atoms in main chains, and blue–green lasing action in a microring cavity by picosecond laser pulse excitation.

II. EXPERIMENT

Two kinds of conducting polymers, poly[(3,6-*N*-2-ethylhexylcarbazolyl)-*co*-diphenylstannane] (SnPhPVK), and poly[(9,9'-dihexylfluorene)-*co*-diphenylstannane] (SnPhFPV), the molecular structures of which are shown in Fig. 1, were studied in the present work. These polymers were synthesized and purified by the method already described.¹⁴ In these polymers, π -conjugations are regularly interrupted along the backbone by Sn atoms, resulting in isolated chromophores which emit blue light in color. These polymers are soluble in common organic solvents such as chloroform and toluene; the installation of a unit with a long Sn–C bond length into a rigid polymer backbone reduces its rigidity, due to the lower barrier to rotation about the Sn–C bonds in the polymer backbone, increasing its solubility.¹⁴

Absorption and PL spectra of polymer thin films prepared by a spin-coating method were measured at room temperature in an evacuated quartz vessel using a Hewlett Packard HP8452A spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. PL quantum efficiency was measured by a system consisting of a mechanical light chopper, an integrated sphere with a photodiode, and a lock-in amplifier.

EL devices with the structure of indium–tin–oxide (ITO)/polymer/aluminum (Al) were fabricated by vacuum deposition of Al onto the polymer thin film on ITO-coated glass substrates. The active area of the EL devices was 4

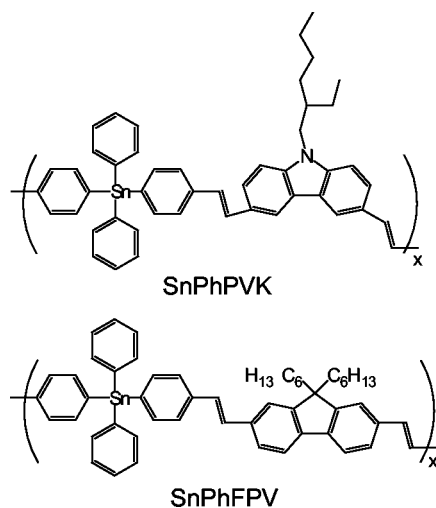


FIG. 1. Molecular structures of conducting polymers with Sn atoms in main chains.

mm². Electrical properties such as current-voltage characteristics and EL spectra were measured using conventional methods.

Electrochemical measurements, such as cyclic voltammetry, were carried out with a three-electrode system consisting of a working electrode with the sample, a platinum counter electrode, and a silver reference electrode in an electrolytic solution of tetrabutylammonium tetrafluoroborate/ acetonitrile using a Hokuto Denko HB-105 function generator and the HA-105 potentiostat.

Time-resolved PL measurements were carried out utilizing a Ti-sapphire mode-lock laser pumped by a cw diode laser as femtosecond pulse-laser system and a second harmonic generator unit. The pulse-laser beam had a pulse width of about 100 fs and pulse rate of 82 MHz. PL was observed using a streak camera, the time resolution of which is about 15 ps. This measurement was carried out at room temperature in an evacuated quartz vessel.

For the PL measurements at high excitation intensities, we used a Nd: yttrium aluminum garnet (YAG) regenerative laser amplifier producing 100 ps pulses with a repetition rate of 1 kHz. This laser light was frequency tripled (355 nm). The pump laser beam was focused by a cylindrical lens onto the polymer thin film, and the emission from the side of the film was detected by a photonic multichannel analyzer (PMA-11, Hamamatsu Photonics Co.) for the measurements of spectral narrowing. Meanwhile, for the measurements of lasing, the pump laser beam was focused by a round lens onto the polymer microring and detected by a spectrometer with a CCD camera. The samples were held in a vacuum cell to avoid degradation by irradiation and oxidation.

The optical fibers were drawn from silica fibers, which were heated and softened with a high-temperature flame. Then fibers with diameters of 15–100 μm could be obtained. To form microring cavities, optical fibers were dipped into chlorobenzene solutions of these polymers. The thickness of the polymer layer was roughly estimated to be less than 1 μm .

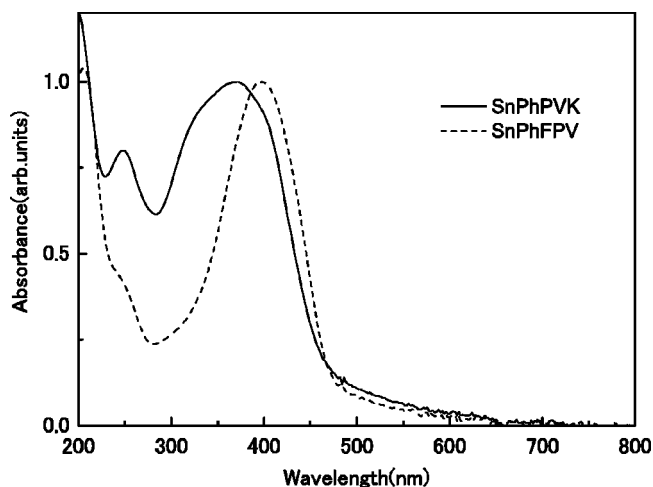


FIG. 2. Absorption spectra of SnPhPVK and SnPhFPV.

III. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of SnPhPVK and SnPhFPV in thin films. The peak wavelengths of absorption in SnPhPVK and SnPhFPV were 372 and 398 nm, respectively, which corresponds to the π - π^* transition of the polymers. From an analysis of the absorption spectral edge corresponding to the highest occupied molecular orbital (HOMO)—the lowest unoccupied molecular orbital gap of the polymers, using the relationship $(h\nu \times \alpha)^2$ vs $h\nu$ (α : absorption coefficient, h : Planck's constant, ν : frequency) under the assumption of direct transition, the bandgap energies of SnPhPVK and SnPhFPV is evaluated as 2.8 and 2.7 eV, respectively.

The top of the valence band, that is, the HOMO, was determined from the observed threshold potential of the electrochemical oxidation in the cyclic voltammogram of the polymers. The threshold potentials of SnPhPVK and SnPhFPV are estimated to be about 0.9 and 1.1 eV below the work function of silver, respectively. From the analysis of the observed absorption spectral edge and the threshold potentials of the electrochemical oxidation, the electronic energy diagrams in these polymers were evaluated as shown in Fig. 3.

When the SnPhPVK and SnPhFPV films were excited by light from a Xe lamp, the wavelengths of which corre-

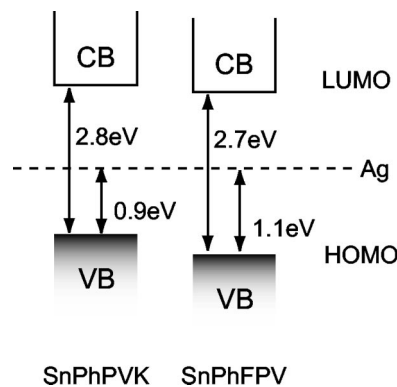


FIG. 3. Electronic energy band diagrams of SnPhPVK and SnPhFPV.

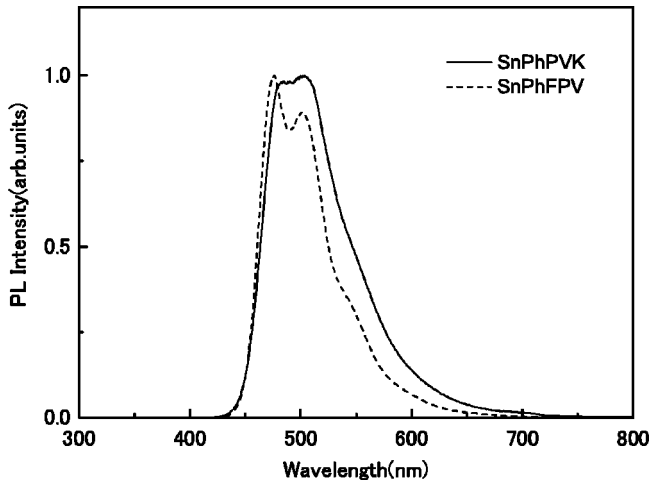


FIG. 4. PL spectra of SnPhPVK and SnPhFPV.

spond to the absorption peaks, strong PL was observed. The PL spectra of SnPhPVK and SnPhFPV are shown in Fig. 4. The peak wavelengths were located at 482 nm for SiPhPVK and 476 nm for SnPhFPV. The emission colors were, therefore, almost blue region for these polymers.

PL quantum efficiencies of the polymer films are evaluated as summarized in Table I, when the laser line at 400 nm of a Ti–sapphire laser was adopted as an excitation source. It should be noted that SnPhPVK demonstrated high efficiency, 39% (photon/photon), in thin film. The efficiency is comparable with previously reported efficiency of blue luminescent conducting polymers.^{15–17}

From time-resolved PL measurements, PL decay time at PL peak wavelength could be approximated by single-exponential decay:¹⁸ $I(t) = I_0 \exp(-t/\tau)$, where $I(t)$ is the PL intensity at time t , I_0 are the initial intensities, and τ are the lifetime constants, respectively. The evaluated PL lifetime constants of the polymers in films are also summarized in Table I. As evident in this table, the polymer with longer lifetime exhibits higher PL quantum efficiency than the results we have already reported.^{17,19}

When the excitation intensity of Nd:YAG laser pulse at 355 nm was increased, the emission spectra of the SnPhFPV film changed as shown in Fig. 5. It is seen that the broad PL spectrum of SnPhFPV obtained at low excitation intensities in Fig. 4 changes at high excitation intensities to a much narrower and stronger emission band peaked at 500 nm with the spectral width of 5 nm. The emission spectral narrowing is accompanied with a nonlinear amplification as illustrated in the inset of Fig. 5. The sharp peak starts to be observed at the input energy of about 2 $\mu\text{J}/\text{pulse}$ and the peak intensity at 500 nm changes superlinearly depending on excitation inten-

TABLE I. Peak wavelengths of absorption and PL, PL efficiencies, and PL lifetimes of conducting polymers with Sn atoms used in this study.

Polymer	Absorption		PL efficiency	
	peak (nm)	PL peak (nm)	(photon/photon)	PL lifetime (ns)
SnPhPVK	348	482	39.2	0.63
SnPhFPV	378	476	24.3	0.44

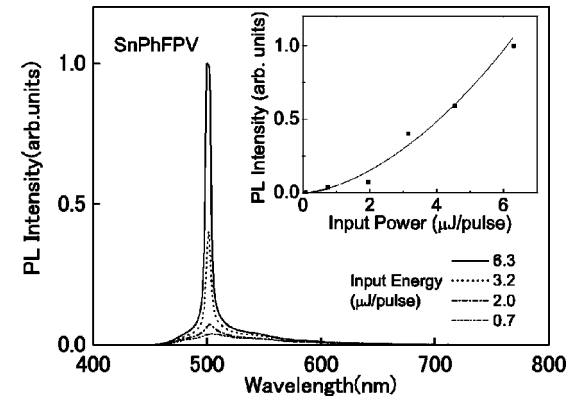


FIG. 5. Optical emission spectra at different excitation pulse energies in SnPhFPV thin film. The inset shows the emission peak intensity dependence on the excitation intensity in SnPhFPV thin film.

sity, as shown in the inset of Fig. 5. Because of higher PL efficiency, spectral narrowing threshold was much lower than that of the polymers with Si atoms in main chains.¹⁷ The spectrally narrowed emission is interpreted to be caused due to the amplified spontaneous emission^{15,20,21} enhanced by the optical waveguiding in the SnPhFPV film.

In the case of LEDs utilizing SnPhPVK and SnPhFPV as emission layers, that is, with a structure of ITO/polymer/Al, strong EL was observed. The LEDs exhibit typical rectifying characteristics. That is, in this case, ITO and Al layers act as hole and electron injecting electrodes, respectively. Each EL spectrum is shown in Fig. 6. The emission peak wavelengths of polymers coincide with those of PL. The current density vs voltage characteristic of SnPhPVK is shown in the inset of Fig. 6. The emission intensity starts to increase at around 6 V.

For the measurements of lasing action, the microring structures as shown in the inset of Fig. 7 were used. A spectrum of the microring lasar emission on SnPhFPV was shown in Fig. 7 as waveguided mode. The outer diameter of the microring D was 90 μm . The bright blue–green striped laser emission all around the ring cavity could be observed, and the spectral width of laser lines was 0.1 nm or less. The

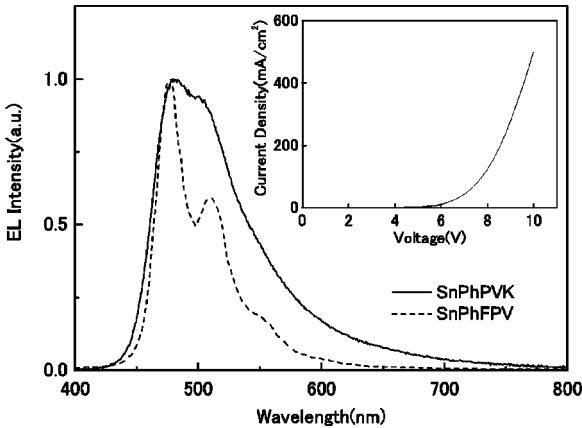


FIG. 6. EL spectra of SnPhPVK and SnPhFPV. The inset shows the current density vs voltage characteristic of SnPhPVK.

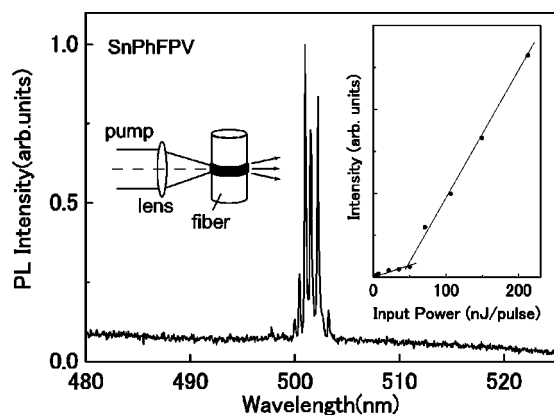


FIG. 7. Lasing spectra of a SnPhFPV microring laser. The insets show a schematic drawing of a photopumped microring laser and the integrated emission intensity vs input pump energy characteristic.

spectral spacing, $\Delta\lambda$, between the laser lines was described as^{22,23}

$$\Delta\lambda = \lambda^2 \pi / D n_{\text{eff}}.$$

From this equation, we calculated the effective refraction index $n_{\text{eff}}=1.77$ with $\Delta\lambda=0.5$ nm, which coincides with the refraction index of ShPhFPV thin film measured by an ellipsometer. It is also noted that the threshold pump energy is about 45 nJ/pulse, as shown in the inset of Fig. 7.

Although some alternating copolymers have already been known as luminescent materials, such blue luminescent alternating copolymers with high quantum efficiencies^{15,16} have hardly been reported. It should be emphasized that copolymers or conducting polymers with hetero atoms in main chains, such as SnPhFPV, could be candidates for blue luminescent materials for organic blue LEDs and blue lasers.

IV. SUMMARY

Optical properties of conducting polymers with Sn atoms in main chains, such as optical absorption, PL and EL, were studied. The electronic energy structures were determined by optical and electrochemical measurements. Strong PL with high quantum efficiency was clarified in the films, and spectral narrowing was observed by pulse excitation of a YAG laser. The multimode blue lasing from microring structure was demonstrated.

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