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Optical and Electrical Properties of Poly(2,5-dialkoxy-1,4-phenylene-alt-2,5-pyridine)

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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. Among various conducting polymers, alternating copolymers with a couple of π-conjugated segments in each monomer unit of polymer main chain are expected to possess unique characteristics and functionalities. Recently, such an alternating copolymer with 2,5-thienylene and 1,4-phenylene units, namely, regioregular poly[3-butyl-2,5-thienylene-alt-1,4-phenylene], was synthesized and demonstrated the solubility in common solvents and the green electroluminescent properties [1]. Alternating copolymers synthesized by the modified synthetic process should also have unique characteristics.

In this paper, we report the optical properties, such as photoluminescence (PL) and spectral narrowing, and the electroluminescent properties of novel alternating copolymer Poly(2,5-dialkoxy-1,4-phenylene-alt-2,5-pyridine) (PHOnPY25).

In this study, we used four kinds of PHOnPY25 with different alkoxy side chain length (n=4, 8, 12, 16), which were synthesized by a method reported elsewhere [2]. These polymers, the molecular structures of which are shown in the inset of Fig. 1, have 2,5-dialkoxy-1,4-phenylene and 2,5-pyridine in a monomer unit. The polymers are soluble in common organic solvents such as chloroform [3].

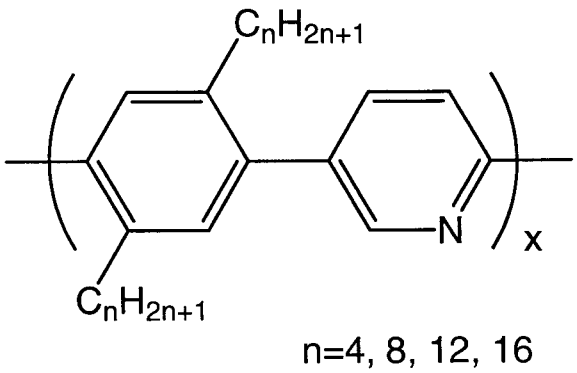


Fig. 1. The molecular structure of PHOnPY25.

Figure 2 shows the absorption spectra of PHOnPY25. As evident from this figure, the absorption edges and peaks are almost the

same for all of the PHOnPY25. That is, the absorption edge is not influenced by the length (n) of the substituted alkoxy moieties. From an analysis of the absorption spectral edge, the band-gap energies of PHOnPY25 are evaluated as 3.0 eV, which are independent of the alkoxy substituent length. The interchain interaction might be quite small in the case of the polymers.

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 PHOnPY25 to be about 1.3 eV below the workfunction of silver.

When the PHOnPY25 films were excited by violet light at 385 nm from a Xe lamp, which was corresponding to the absorption peak wavelength, strong blue PL was observed. The spectra of PHOnPY25 are shown in Fig. 2. The peak wavelengths are located at 430-440 nm for PHO4PY25, PHO8PY25 and PHO12PY25, and at 500 nm for PHO16PY25. PL quantum efficiencies of the polymer films are evaluated to be about 20%, when the laser line at 363.7 nm of an Ar^+ laser is adopted as an excitation source. Such efficiency is comparable with previously reported efficiency of blue luminescent conducting polymers [4].

For the PL measurements at high excitation intensities, we used a laser beam with 600 ps pulses with the energy per pulse ranging from 1 to 110 μJ, provided by a nitrogen laser, the wavelength of which was 337.1 nm. When the excitation intensity was increased, the emission spectra of PHO12PY25 film changed as shown in Fig. 3(a). It is seen that the broad PL spectrum obtained at low excitation intensities changes at high excitation intensities to a much narrower and stronger emission band peaked at 460 nm with the spectral width of 5 nm. The emission spectral narrowing is accompanied by a

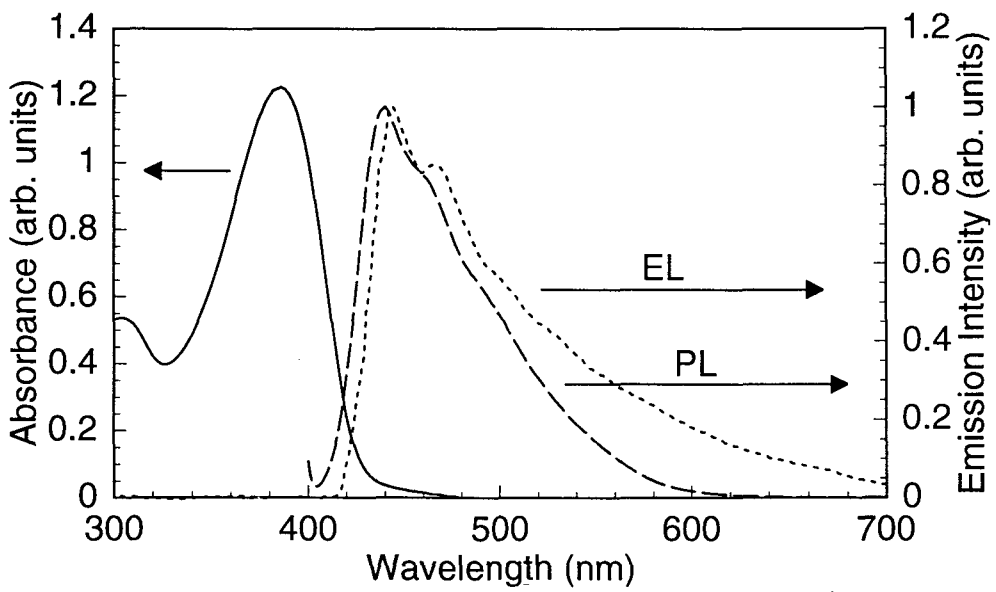
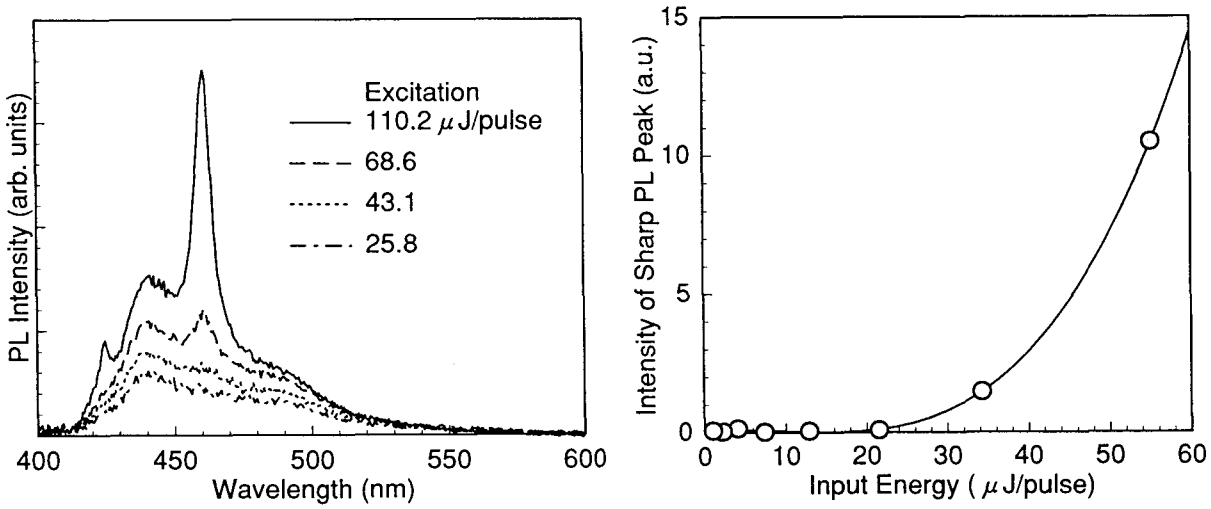


Fig. 2. Absorption, PL and EL spectra of PHO8PY25.



(a) (b)

Fig. 3. (a) Optical emission spectra at different excitation pulse energies in PHO12PY25 thin film. (b) Emission peak intensity dependence on the excitation intensity in PHO12PY25 thin film.

nonlinear amplification as illustrated in Fig. 3(b), the PL intensities of which are subtracted by the linearly increasing factor of PL intensities. As apparent in Fig. 3, the sharp peak starts to be observed at the input energy of 20 μJ/pulse and the intensity of the peak at 460 nm changes its dependence on excitation intensity to superlinear.

In the case of LEDs utilizing PHOnPY25 as emission layers, that is, with a structure of ITO/PHOnPY25/Al, strong blue electroluminescence were observed. The LEDs exhibit typical rectifying characteristics. That is, in this case, ITO and Al layers act as hole and electron injecting electrodes, respectively. The emission intensity starts to increase at around 15 V. The driving voltages tended to increase with increasing polymer thickness. The emission intensity increased monotonically with increasing injection current.

By applying a positive bias voltage of, for example, 20 V to the PHOnPY25 LEDs, a bright blue emission was obtained at 77 K, the EL spectra of which is shown in Fig. 2. The emission peak wavelengths of PHOnPY25 are around 430-440 nm, which coincide with those of PL.

In conclusions, optical properties of PHOnPY25, such as absorption spectra, PL, spectral narrowing and EL, were studied. The electronic energy structures of PHOnPY25 were determined by optical and electrochemical measurements. Spectral narrowing of PL were observed from PHOnPY25 films by photo-excitation. Intense EL was also demonstrated in the LEDs of PHOnPY25.

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