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Optical and luminescent propertis of fluorene-pyridine copolymers

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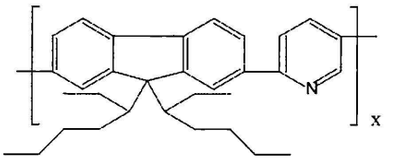
The use of π-conjugated conducting polymers as functional materials has attracted much attention from the point of view of basic science and applications, because of their high processability, stability, and promising electrical and optical properties[1]. Among various conducting polymers, alkyl- or alkoxyl-substituted polymers, such as poly(3-alkylthiophen)[2], poly(9,9-dialkylfluorene) (PDAF)[3,4], poly(*p*-phenylene) (PPP) derivative[5,6,7] and poly(2,5-dialkoxy-*p*-phenylene vinylene)[8] are the most attractive materials, because of their solubility in common solvent, and their high luminescent quantum efficiency.

Utilizing conducting polymers with relatively large band gaps, such as PDAF and its derivatives, polymer blue light-emitting diodes (LEDs) and polymer blue lasers could be realized.

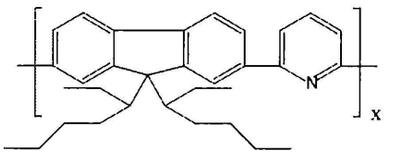
On the other hand, alternating copolymers with a π-conjugated segment and a pyridine, which contains N atom, in each monomer unit of polymer main chains are expected to possess unique characteristics and functionalities. Recently copolymers such as poly(2,5-dioctylkoxy-1,4,phenylene-alt-2,5-pyridine)[6,7], poly(2,5-dioctylkoxy-1,4-phenylene-alt-2,6-pyridine)[6], were synthesized and demonstrated the blue electroluminescent (EL) properties. Furthermore, they were highly soluble in common solvents and high-quality thin films could be obtained in wet process. Copolymers synthesized by the modified synthetic process should be also have another π-conjugated segment and a possibility to exhibit unique luminescent properties. Indeed, Ng *et al.* reported on their success in the synthesis of copolymers with pyridine in main chains, and demonstated reduction of the lowest molecular orbital (LUMO) level.

In this study, we report the optical properties, such as photoluminescence (PL), spectral narrowing of PL, and the EL properties of fluorene-pyridine copolymers.

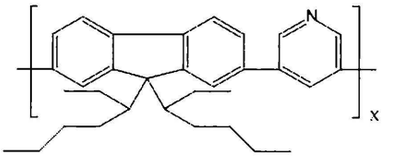
Three kind of conducting polymers, poly[(9,9-di-{ethylhexyl}-fluorenyl-2,7-diyl)-*co*-(2,5-pyridine)](PDEHFP-25), poly[(9,9-di-{ethylhexyl}-fluorenyl-2,7-diyl)-*co*-(2,6-pyridine)] (PDEHFP-26), and poly[(9,9-di-{ethylhexly}-fluorenyl-2,7-diyl)-*co*-(3,5-pyridine)] (PDEHFP-35), the molecular structures of which are shown in Fig. 1, were studied in the present work. These polymers are soluble in common organic solvents such as chloroform and toluene.



PDEHFP-25



PDEHFP-26



PDEHFP-35

Fig. 1: Molecular structures of fluorene-pyridine copolymers.

Fig.2 shows the absorption spectra of these polymers in thin film. As evident from this figure, the absorption peaks of PDEHFP-26, 35 are shifted to shorter wavelength than that of PDEHFP-25. From an analysis of absorption spectral edges, the band-gap energies of PDEHFP-25 , PDEHFP-26 and PDEHFP-35 are evaluated as 2.9 eV, 3.2 eV and 3.4 eV, respectively.

The top of the valence band, that is, the HOMO, is determined from the observed threshold potential of the electrochemical oxidation in the cyclic voltammogram of the polymers. The threshold potential of PDEHFP-25, PDEHFP-26 and PDEHFP-35 are estimated to be about 1.2 eV, 1.3 eV and 1.4 eV below the work function of silver, respectively. From the analysis of the observed absorption spectral edge and threshold potential of the electrochemical oxidation, the electronic energy diagram in these polymers are evaluated.

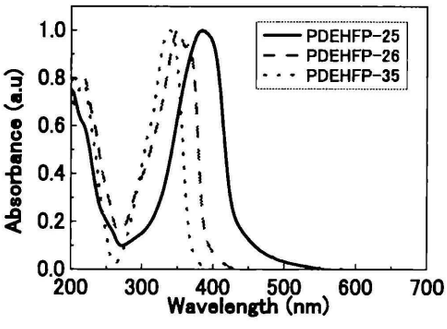


Fig. 2: Absorption spectra of fluoren-pyridine copolymers.

When these polymer films are excited by light from a Xe lamp, the wavelength of which correspond to the absorption peaks, strong PL was observed. The PL spectra of these polymers are shown in Fig.3. The peak wavelengths were located at 476 nm for

PDEHFP-25, 406 nm for PDEHFP-26 and 416 nm for PDEHFP-35. The emission colors were blue region for these polymers.

PL quantum efficiencies of polymer films were evaluated as 21.3 for PDEHFP-25, 36.5 for PDEHFP-26 and 43.6 % (photon/photon) for PDEHFP-35, when the laser line at 355 nm of Nd:YAG laser was adopted as an excitation source. It should be noted that PDEHFP-35 demonstrated high efficiency in thin film. The efficiency is comparable with previously reported efficiency of blue luminescent conducting polymers[7].

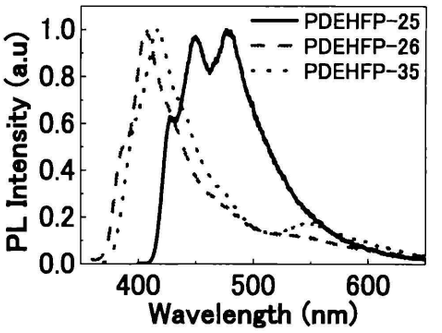


Fig. 3: PL spectra of fluoren-pyridine copolymers.

When the excitation intensity of Nd:YAG laser pulse at 355 nm was increased, the emission spectra of the PDEHFP-35 film changed as shown in Fig.4. It is seen that the broad PL spectrum of PDEHFP-35 obtained at low excitation intensities in Fig. 3 changes at high excitation intensities to a much narrower and strong emission band peaked at 410 nm with the spectal width of 9 nm. The emission spectral narrowing is accompanied with a nonlinear amplification as illustrated in the inset of Fig. 4. The sharp peak starts to be observed at the input energy of about 2.4μJ/pulse and the peak intensity at 410 nm changes superlinearly depending on excitation intensity, as shown in the inset of Fig.4. The spectrally narrowed emission is interpreted to be caused due to the amplified spontaneous emission [9] enhanced by the optical waveguiding in the PDEHFP-35 film.

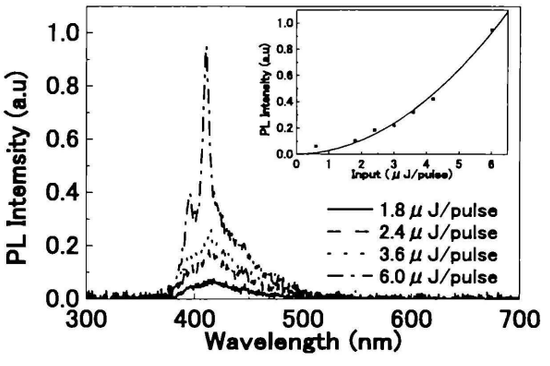


Fig. 4: Optical emission spectra at different excitation pulse energies in PDEHFP-35 thin film. Inset shows the emission peak intensity dependence on the excitation intensity in PDEHFP-35 film.

In the case of LEDs utilizing these polymers as emission layers, that is, with a structure of ITO/PEDOT:PSS/polymer/MgAg, strong EL was observed. The LEDs

exhibit typical rectifying characteristics. That is, in this case, ITO and MgAg layers act as hole and electron injection electrodes, respectively. Each EL spectrum is shown in Fig.5. The emission peak wavelength are roughly in accordance with those of PL. The emission intensity starts to increase at around 15 V.

It should be emphasized that copolymers, such as PDEHFP-35, could be candidates of blue luminescent materials for organic blue LEDs and lasers.

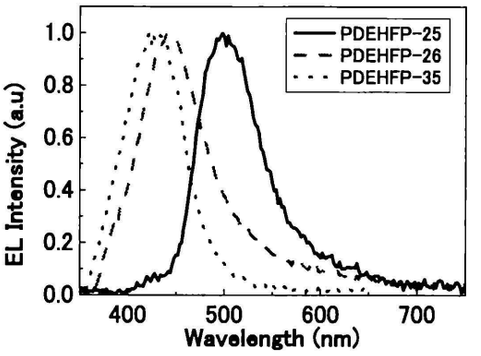


Fig. 5: EL spectra of fluoren-pyridine copolymers.

In conclusion, optical properties of fluorene-pyridine copolymers, 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 observed by pulse excitation of a Nd:YAG laser.

References

[1] K. Yoshino, M. Onoda, and T. Kawai, Optoelectronics, **5** (1990) 1

[2] Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, Jpn. J. Appl. Phys., Part 2 **30**, L1938 (1991)

[3] M. Fukuda, K. Sawada, and K. Yoshino, Jpn. J. Appl .Phys., Part 2 **28**, L1433 (1989)

[4] Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, Jpn. J. Appl. Phys., Part 2 **30**, L1433 (1991)

[5] M. Hamaguchi, H. Sawada, J. kyokane, and K. Yoshino, Chem. Lett. **1996**, 527 (1996)

[6] S. –C. Ng, H. F. Lu, H. S. O. Chan, A. Fujii, K. Yoshino, Adv. Mater. **12**, (2000), 1122

[7] A. Fujii, R. OOtake, T. Fujisawa, M. Ozaki, Y. Ohmori, T. Laga, H. –F. Lu, H. S. O. Chan, S,-C. Ng, and K. Yoshino, Appl. Phys. Lett., **77**, (2000) 660

[8] M. Hamaguchi, and K. Yoshino, Jpn. J. Appl. Phys., Part 2 **33**, L1478 (1994)

[9] M. N Shkunov, R. Österbacka, A. Fujii, K. Yoshino, and Z. B. Vardeny, Appl. Phys. Lett., **74**, (1999) 1648