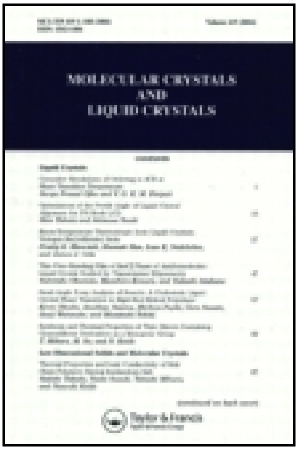

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Photoluminescence, Electroluminescence, Lasing and Novel Characteristics in Photonic Crystal, Synthetic Opal, of Conducting Polymers, Polyacetylene Derivatives

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Photoluminescence, Electroluminescence, Lasing and Novel Characteristics in Photonic Crystal, Synthetic Opal, of Conducting Polymers, Polyacetylene Derivatives

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Photoluminescence (PL) intensity and spectrum are strongly dependent on substituents of conducting polymers, such as polyacetylene derivatives. Intense PL and electroluminescence (EL) have been observed in di-substituted polyacetylene derivatives. Novel EL characteristics have also been found in EL devices with aligned conducting polymers and also of various electrode configurations. Spectral narrowing and lasing have been observed in conducting polymers with micro-ring structures and also in photonic crystals upon relatively low optical excitation.

Keywords: photoluminescence; electroluminescence; lasing; photonic crystal; synthetic opal; polyacetylene derivatives

INTRODUCTION

Conducting polymers with highly extended π-electron systems in the main chains have attracted much attention not only from fundamental scientific view points but also from practical interest, because various new functional applications of conducting polymers have been proposed. Among various applications, electroluminescence (EL) utilizing highly fluorescent conducting polymers is one of the most promising one.

Various highly fluorescent conducting polymers have been prepared so far, such as poly(*p*-phenylenevinylene)[1], poly(3-alkylthiophene)[2], poly(alkylfluorene)[3], poly(2,5-dialkoxy-*p*-phenylenevinylene)[4] and poly(*p*-phenylene) derivatives[5] etc. We have also reported strong EL even in polyacetylene (PA) derivatives[6-8] which have not been concerned as light emissive materials at early stage of research because of reports of non-luminescence in trans-PA and its interpretation with soliton model[9], though weak PL was observed in near infrared and the interpretation with soliton model was pointed out to be not appropriate[10, 11]. In these conducting polymers, fluorescence characteristics are strongly dependent on the molecular structure of substituents.

In this paper, we report such strong effects of substituents on PL and EL characteristics utilizing polyacetylene derivatives as examples. Unique characteristics of EL devices with highly oriented conducting polymers[12] and

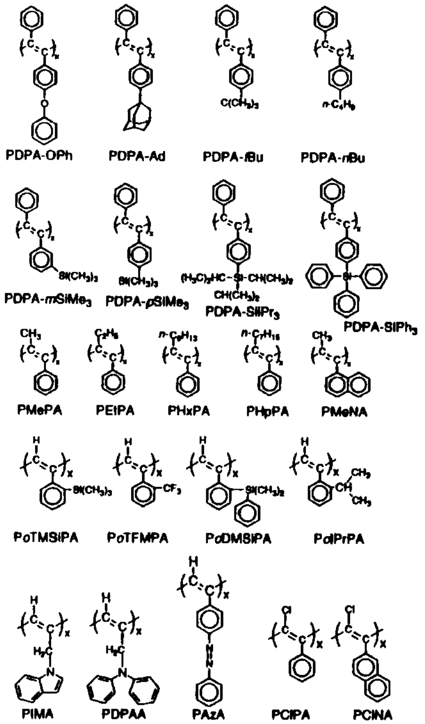

FIGURE 1 Molecular structure of PA derivatives.

specific electrode configuration[13] and also spectral narrowing and lasing upon optical excitation are also discussed[13-15].

EXPERIMENTAL

Molecular structures and their abbreviated names of polyacetylene derivatives specially examined to clarify the effects of substituents are shown in Fig. 1. Preparation and purification methods of these conducting polymers were already reported in previous papers. These conducting polymers are soluble in conventional solvents such as chloroform and thin films of these conducting polymers were prepared by spin coating of chloroform solution of the conducting polymer on appropriate substrates.

Absorption and PL spectra of films on quartz plates were measured under vacuum using a spectrophotometer (HP8542 or Hitachi 330) and a fluorescence spectrometer (Hitachi F-2000), respectively.

Electrochemical measurements such as cyclic voltammetry to evaluate electronic states of conducting polymers were carried out utilizing a potentiostat (Hokuto-Denko HA-501) and a programmable function generator (Hokuto-Denko HB-105) in a dry box filled with argon gas. A three-electrode electrochemical cell with Ag wire, a sample film on ITO (In-Sn oxide) coated glass and a Pt plate were used as reference electrode, working electrode and counter electrode, respectively. The electrochemical cell was filled with purified acetonitrile containing dried tetrabutylammonium tetrafluoroborate as a supporting salt. In situ absorption spectrum measurements during electrochemical doping was carried out by putting the electrochemical cell with the sample film on ITO in the sample chamber of a spectrophotometer (Hitachi 330).

For preparation of the EL devices a conducting polymer film was formed on an ITO-coated glass plate by the spin coating method utilizing chloroform solution of concentration of 10^{-2} mol/l and then Mg-In alloy or Al were deposited by vacuum evaporation on the top of the film. An ITO-coated glass fiber of 125 μm in a diameter was also used as substrates on which conducting polymer layer was formed by dipping the fiber in the chloroform solution of the conducting polymer and then Al was deposited in vacuum to construct a cylindrical configuration of EL device. EL characteristics were studied either under vacuum at room temperature (RT) or in liquid nitrogen by a method reported previously.

For the study of spectral narrowing of PL, laser beams of 532 nm and 355 nm with 10 ns and 100 ps pulse widths produced by second harmonic generation (SHG) and third harmonic generation (THG) of Nd-YAG lasers were used. Spectral narrowing and lasing of conducting polymers infiltrated in

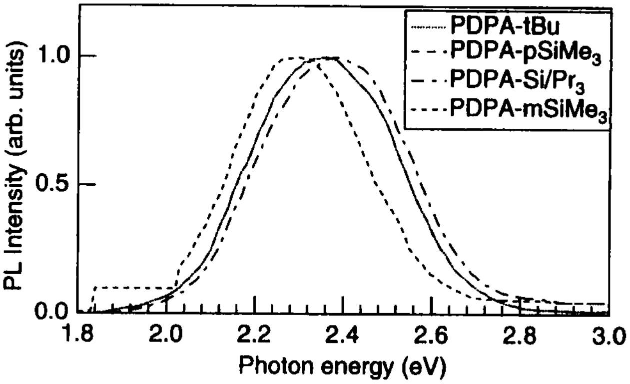

FIGURE 2 PL spectra of PDPA derivatives.

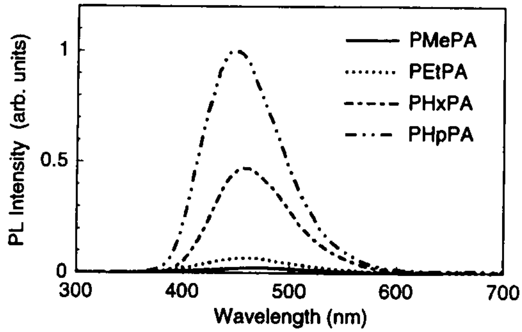

FIGURE 3 PL spectra of PAPA derivatives.

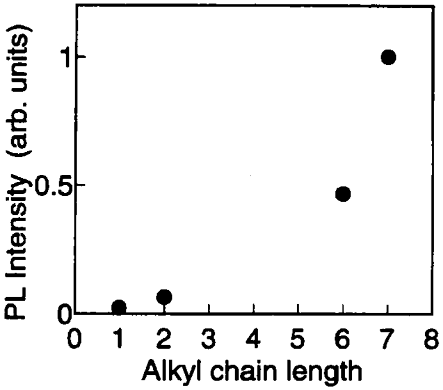

FIGURE 4 Alkyl chain length dependence of PL of PAPA.

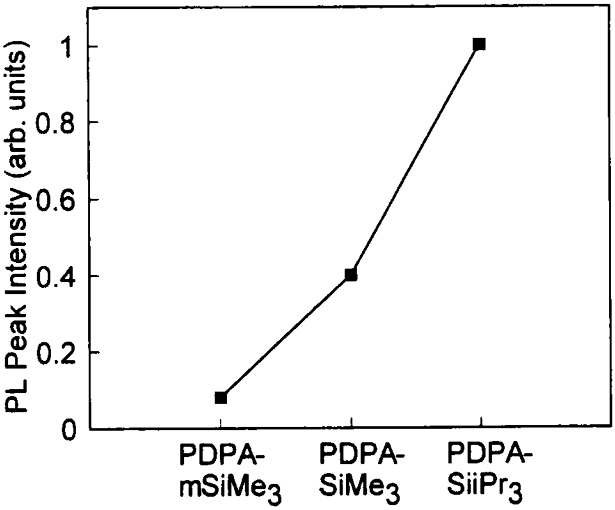

FIGURE 5 Substituent dependence of PL of PDPA.

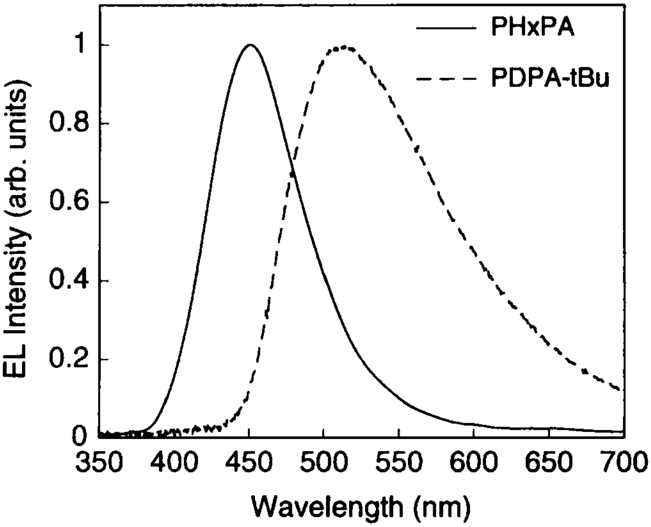

FIGURE 6 EL spectra of PDPA and PAPA.

synthetic opals, photonic crystals, made of regularly stacked SiO_2 spheres of 250 nm, 210 nm and 160 nm in diameter were also studied[16].

RESULTS AND DISCUSSION

Dependences of PL and EL Characteristics on Substituents of Polyacetylene Derivatives

Electronic energy states such as band gap and location of excited states in energy are strongly influenced by the molecular structure of substituents. Therefore, absorption spectra and PL characteristics are strongly substituents dependent.

The band gap of mono-substituted PA such as PoTMSiPA, PoDMPSiPA, PoiPPA, PoTFMPA is around 2 eV and therefore they are candidates of the EL of red in color. Though we can observe extremely weak red PL and EL in these mono-substituted PAs, they are practically too weak for practical use. That is, we can conclude that usual mono-substituted PAs are effectively nonluminescent.

On the contrary, di-substituted PAs are highly luminescent. For example, di-phenylsubstituted PA derivatives (PDPA) such as PDPA-Ad, PDPA-tBu, PDPA-nBu, PDPA-m$SiMe_3$, PDPA-p$SiMe_3$, PDPA-$SiiPr_3$, PDPA-$SiPh_3$ have band gaps around 2.55-2.75 eV and exhibited strong green PL as shown in Fig. 2 and di-substituted PAs of poly(1-alkyl-2-phenylacetylene)(PAPA) series such as PMePA, PEtPA, PHxPA and PHpPA have band gaps of around 3.3-3.5 eV and exhibit intense blue PL as shown in Fig. 3.

These di-substituted PA are all highly emissive, in contrast to mono-substituted PA. Especially in the case of PAPA series of PAs, PL intensity increased remarkably with increasing alkyl chain length of the substituent as evident in Fig. 4. Similarly in the case of PDPA series of PAs, PL intensity was also strongly dependent on the substituents as shown in Fig. 5 as examples for Si-phenyl types of substituents.

These di-substituted PAs also exhibited intense EL. That is, PDPA and PAPA series of polymers exhibited strong green and blue ELs as shown in Fig. 6, respectively. EL intensity was also strongly dependent on the molecular structure of substituents just as the case of PL. That is, EL of PAPA series of polymers increased drastically with increasing alkyl chain length.

These experimental results of strong PL and EL in disubstituted PAs suggest that the excited states are dependent on the substituents. That is, in di-substituted PAs 2^1Ag state may be located at higher energy than 1^1Bu state, contrary to non-substituted PA, in which 2^1Ag is located lower than 1^1Bu in energy. In most mono-substituted PAs also 2^1Ag state may be lower than 1^1Bu in energy. The relaxation of the main chain configuration after excitation by light irradiation or charge injections may also be dependent on the substituent.

In polymer mixture films of PDPA and PAPA both PL and EL intensity and spectrum depend strongly on their concentration. For example in the case of the mixture film of PDPA-nBu and PHxPA the emission peak shift to lower energy upon mixing of small amount of PDPA-nBu in PHxPA and the spectrum is confirmed to be composed of overlapped peaks originating from PDPA-nBu and PHxPA. This results can be explained in terms of relative energy of excited states of both polymers by taking the energy transfer from excited PHxPA to PDPA-nBu into consideration.

It should also be mentioned that EL was observed not only in the device with a structure of parallel electrodes configuration such as Mg-In/conducting polymer/ITO and Al/conducting polymer/ITO but also in the device with cylindrical electrode configuration with Al/conducting polymer/ITO on optical fiber.

We have also realized polarized EL utilizing aligned conducting polymer by extremely simple technique. That is, conducting polymer prepared by spin coating on ITO glass was rubbed unidirectionally by cloth just as the case of a rubbing treatment of ITO surface in liquid crystal devices for alignment of liquid crystal molecules. On the rubbed conducting polymer such as poly(2,5-dinonyloxy-1,4-phenylenevinylene) Mg-In was vacuum deposited. Upon application of negative bias voltage to Mg-In side relative to ITO, strong emission polarized in the rubbing direction was obtained. These polarized EL is useful for the back light of liquid crystal display devices.

Spectral Narrowing and Lasing upon Optical Excitation

We have also studied laser emission from highly fluorescent polymers upon optical excitation.

Strong PL in di-substituted PA such as in PDPA-nBu with quantum yield exceeding 60% suggests that di-substituted PAs are good candidate for high optical gain in films and lasing upon intense optical excitation. Measurements have been carried out utilizing SHG and THG lights of Nd:YAG laser.

Figure 7 shows the change of emission spectra from PDPA-nBu film with increasing excitation intensity. As evident in this figure, remarkable spectral narrowing has been observed. Similar spectral narrowing was observed also in other PDPA series of PA derivatives, indicating stimulated emission and lasing.

In PAPA series of PA derivatives, however, such remarkable spectral narrowing was not so remarkable in blue range which may be due to either excited state absorption or poor film quality. To realize lasing, the introduction of optical feed back system such as formation of a cavity with mirrors is useful., in general. We checked it utilizing cylindrical micro-cavity formed by conducting polymers such as di-substituted PA thin films deposited around optical glass fibers. The polymer layer acts as a wave guide forming a ring resonator around the glass fiber. In general, the micro-ring system utilizing cylindrical configuration, both wave guided mode (WM) and whispering gallery mode

(WG) can propagate either in polymer films or in fiber close to the surface

In the emission spectrum of PDPA-Si(iPr)$_3$ films formed on a optical fiber of 125 nm in diameter upon 355 nm light irradiation, multi-mode laser spectrum was observed. The intermodal spectral spacing of about 16-16.7 cm^{-1} corresponds to effective refractive index of about 1.59-1.52, which is reasonable value in this polymer. It should also be noted that the mode structure in this figure is periodically modulated which may also be attributed to the resonant coupling between WM and WGM in the ring cavity.

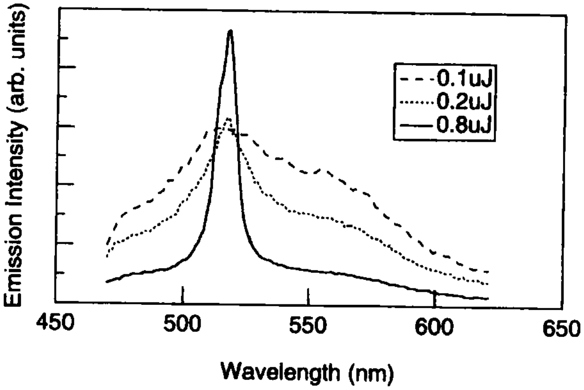

FIGURE 7 Optical emission spectra at different excitation pulse energies in PDPA-nBu.

Characteristics of Conducting Polymer in Synthetic Opal as Photonic Crystal

We have also studied conducting polymers such as di-substituted PAs, poly(2,5-dialkoxyphenylene vinylene) (RO-PPV) in synthetic opals as photonic crystals.

In the reflection spectra of a synthetic opal, that is a purple opal made of SiO$_2$ spheres of 160 nm in diameter, a sharp diffraction peak was observed. Similar diffraction peaks were also observed in synthetic opals, red opal and green opal with SiO$_2$ spheres of 250 nm and 210 nm, respectively. The periodicity evaluated from the diffraction spectrum well coincided with that observed in the electron micrograph. The reflection spectrum of opal infiltrated with conducting polymer PDPA-nBu is also studied. The diffraction peak does not shift with infiltration of conducting polymer but PL originating from conducting polymer such as PDPA-nBu and RO-PPV is overlapping with the diffraction peak, supporting well infiltration of conducting polymer in the nano-space of the opal.

The emission spectra of the green opal infiltrated with conducting polymers such as RO-PPV and PDPA-nBu with increasing the excitation intensity of SHG and THG of Nd:YAG show remarkable increase in intensity and spectral narrowing shown in Fig.8 in RO-PPV infiltrated green opal as an example. Similar spectral narrowing of the emission with increasing excitation intensity was also observed in conducting polymers infiltrated in other opals, purple opal and red opal also in many other conducting polymers in synthetic opals.

It should be mentioned that spectral narrowing occurs at excitation intensity much lower than the threshold of the same conducting polymer in toluene. These results indicate that the observed spectral narrowing and remarkable enhancement of sharp emission peak originates from stimulated emission,

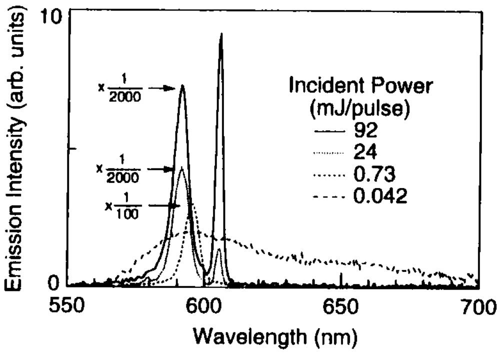

FIGURE 8 Emission spectra of synthetic opal infiltrated with conducting polymer, RO-PPV as function of optical excitation intensity measured with the system of spectral resolution of 3 nm.

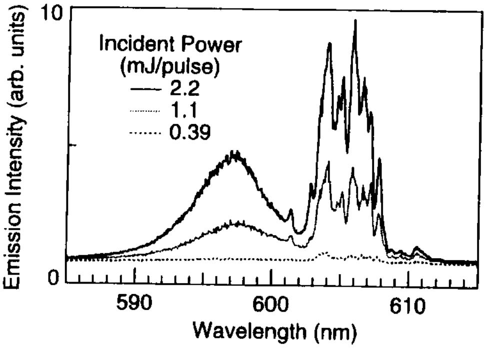

FIGURE 9 Emission spectra of synthetic opal infiltrated with conducting polymer, RO-PPV as function of optical excitation intensity measured with the system of spectral resolution of 0.3 nm.

resulting in lasing.

The results indicated in Fig.8 was observed with a measuring system of spectral resolution of 3 nm. However, in the case of observation with the system of better spectral resolution of 0.3 nm, much narrow emission peaks were revealed as shown in Fig. 9, indicating multi-mode emission.

Though further detailed experiments are necessary for clear discussion, the present experimental results indicate that the three dimensional periodic structure of synthetic opals as photonic crystals influences remarkably on the feed back system in lasing. The possibility of random laser also must be taken into consideration at this stage of experiment.

ACKNOWLEDGEMENT

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