



Title	Luminescent Characteristics of Poly(diphenylacetylene) Derivatives with Substituents Containing Si and Ge Atoms
Author(s)	Nishihara, Yusuke; Hidayat, Rahmat; Fujii, Akihiko et al.
Citation	電気材料技術雑誌. 2001, 10(1), p. 54-63
Version Type	VoR
URL	https://hdl.handle.net/11094/81640
rights	
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Luminescent Characteristics of Poly(diphenylacetylene) Derivatives with Substituents Containing Si and Ge Atoms

Yusuke NISHIHARA, Rahmat HIDAYAT, Akihiko FUJII, Masanori OZAKI and Katsumi YOSHINO

Department of Electronic Engineering, Graduate School of Engineering, Osaka University,
2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

S. M. Abdul KARIM, Toshio MASUDA

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Optical properties such as photoluminescence (PL) and electroluminescence (EL) of poly(diphenylacetylene) (PDPA) derivatives with substituents containing silicon and germanium atoms have been studied. PDPA derivatives exhibited highly efficient PL and PL spectral narrowing originated from amplified spontaneous emission (ASE) in the case of high excitation. The peak wavelength of PL spectra depends on the positions of substitution and the atoms (silicon or germanium) of the substitution. EL has also been observed from PDPA derivatives sandwiched between magnesium-silver alloy cathode and indium-tin-oxide anode. PL decay has also been confirmed to be dependent on the position of the substituents and the hetero-atoms in the substituents. These characteristics have been interpreted in terms of the effects of substituent properties and their positions on the conformation of the main chains and electronic energy schemes.

KEYWORDS : conducting polymers, photoluminescence, electroluminescence, polyacetylenes, disubstituted polyacetylenes

Si、Ge 原子含有置換基を有するポリジフェニルアセチレンの発光特性

西原雄祐、ラフマツト・ヒダヤット、藤井彰彦、尾崎雅則、吉野勝美

大阪大学大学院工学研究科電子工学専攻
〒565-0871 大阪府吹田市山田丘 2-1

アブドゥル・カリム、増田俊夫

京都大学大学院工学研究科高分子化学専攻
〒606-8501 京都市左京区吉田本町

Si や Ge 原子を含む置換基を有するポリジフェニルアセチレン(PDPA)の電界発光(EL)や蛍光(PL)及び高強度励起時における蛍光スペクトルナローイングのような光学的特性については以前から研究されている。このような PDPA は高い蛍光効率を示し、蛍光のピーク波長は置換基の原子の種類(Si や Ge)及び、位置に大きく依存している。また、陽極を ITO、陰極を MgAg としてサンドイッチ構造とした EL も観測されている。蛍光寿命においても同様に、置換基の原子の種類及び、位置に大きく依存している。これらの特性は置換基の性質や主鎖のコンフォメーション及び、エネルギーバンド図によって説明される。

1.introduction

Recently, conducting polymers with extended π -electron systems in the main chains have attracted attention not only from the fundamental viewpoints but also from the practical interest for various functional applications such as capacitors and display devices.¹⁾ Among various conducting polymers, polyacetylene has the simplest molecular structure and has been widely studied since the finding of the insulator-metal transition upon doping, and its interpretation with soliton model.^{2,3)} However, the fluorescent characteristics of polyacetylene have not attracted much attention, because Lauchlan et al. reported that trans-polyacetylene was intrinsically non-emissive and it could be explained by soliton model.⁴⁾

On the other hand, we reported that even in trans-polyacetylene weak photoluminescence (PL) was observed in infrared region,⁵⁾ and the results could not be explained simply by soliton model. We interpreted the results by taking the relative energy of the excited state 1Bu and 2Ag into consideration instead of soliton model.^{6,7)}

Recently, we reported that even strong green and blue PLs were observed in disubstituted polyacetylenes, poly(diphenylacetylene)

(PDPA) series and polyalkylphenylacetylene (PAPA) series.^{8,9)} Green and blue electroluminescence (EL) were also observed in these disubstituted polyacetylene series.^{9,10)} Besides, it was reported that PDPAs with substituents containing a hetero-atom such as silicon (Si) also possessed efficient emission characteristics. The effects of hetero-atoms in the PDPA derivatives to π -conjugation should be of interest for the investigations of the emission mechanisms and electronic structures and for the device applications.

In this paper, we report that the emission characteristics of PDPA series are dependent on the position of the substituents and also on the molecular structures of the substituents, especially containing the hetero-atoms such as Si and germanium (Ge).

2.Experiment

Substituted PDPAs such as poly(1-phenyl-2-*m*-(trimethylsilyl) phenylacetylene) (PDPA-mSiMe₃), poly(1-phenyl-2-*m*-(trimethylgermyl) phenylacetylene)(PDPA-mGeMe₃), poly(1-phenyl-2-*p*-(trimethylsilyl)phenylacetylene)(PDPA-pSiMe₃), poly(1-phenyl-2-*p*-(tri-phenylsilyl)phenylacetylene)(PDPA-pSiPh₃), the molecular structures

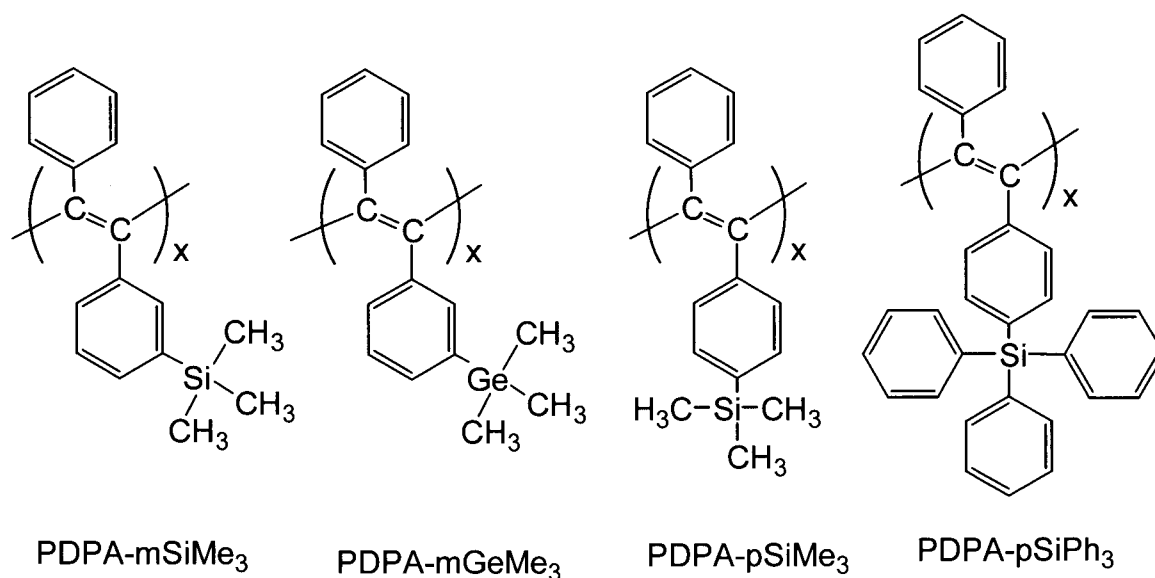


Fig.1: Molecular structures of PDPA derivatives used in this study.

Table I. Peak wavelengths of absorption and PL and PL efficiencies of PDPA derivatives used in this study

Polymer	Absorption peak (nm)	PL peak (nm)	PL efficiency (photon/photon)
PDPA-mSiMe ₃	434	548	27
PDPA-mGeMe ₃	422	540	26
PDPA-pSiMe ₃ ^{8,9)}	422	523	25
PDPA-pSiPh ₃	406	559	28

of which are shown in Fig. 1, were studied in the present work. The synthesis and purification of these PDPAs were described elsewhere.^{11,12)} These PDPAs are soluble in common organic solvents such as chloroform and toluene.

Absorption and PL spectra of PDPAs in solutions and 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 an Ar⁺ laser, a mechanical light chopper, an integrated sphere with photodiode and a lock-in amplifier. The nonlinear emission from the PDPA derivatives film was measured using a charge coupled detector (CCD) and a photomultichannel analyzer (PMA). We used a laser beam as a pump beam with 150ps pulses with the energy per pulse ranging from 0.1 to 20mJ/pulse provided by a Ti:Sapphire mode-locked laser, the wavelength of which was 400nm. The pump beam was focused by a cylindrical lens onto PDPA films.

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.

EL devices with the structure of indium-tin-oxide(ITO)/PDPA derivative/magnesium-silver alloy (MgAg) were fabricated by vacuum deposition of the alloy of MgAg onto PDPA derivative film on ITO-coated glass substrates. The active area of the EL devices was 4 mm². Electrical properties such as current-voltage characteristics and EL spectra were measured using conventional methods, which were described previously.^{13,14)}

Time resolved PL measurements were carried out utilizing a femtosecond pulse-laser system (a Ti-Sapphire mode-lock laser pumped by a cw diode laser) 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, which determined the resolution of the measurement to be about 15 ps. This measurement was carried out at room temperature in an evacuated quartz vessel.

3. Results and Discussion

Figure 2 shows absorption and PL spectra of PDPA-mSiMe₃ and PDPA-mGeMe₃ in films. The peak wavelengths of absorption and PL were 434 nm and 548 nm in PDPA-mSiMe₃ and 422 nm and 540 nm in PDPA-mGeMe₃, respectively. It

should be noted that the absorption edge and the PL peak of PDPA-mSiMe₃ in film were located at longer wavelength than those of PDPA-mGeMe₃. Similar redshifts of absorption edge and PL peak were also observed in PDPA-mGeMe₃ solution. Though the origin of these relatively small difference is not clear at this stage, the difference of electronegativity of Si and Ge atoms or the difference in effective conjugation of PDPA-mSiMe₃ and PDPA-mGeMe₃ may have influenced.

Both PLs of PDPA-mSiMe₃ and PDPA-mGeMe₃ were strong green emissions, and the PL efficiency of PDPA-mSiMe₃ was nearly the same with that of PDPA-mGeMe₃, 26-27% (photon/photon), as summarized in Table I.

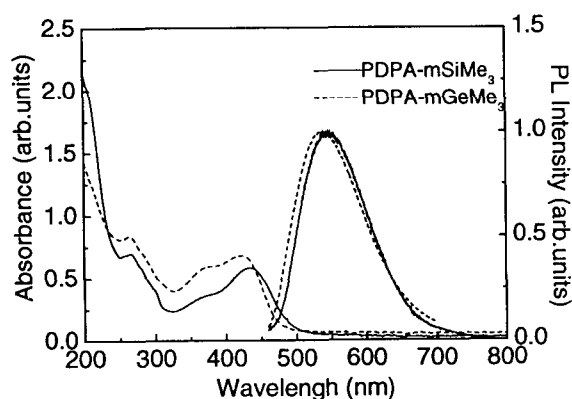


Fig.2: Absorption and PL spectra of PDPA-mSiMe₃ and PDPA-mGeMe₃

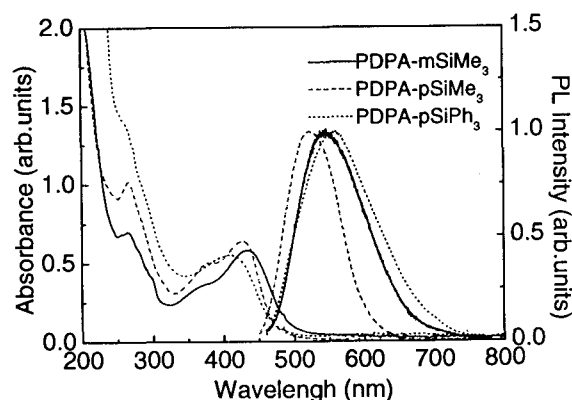


Fig.3: Absorption and PL spectra of PDPA-mSiMe₃, PDPA-pSiMe₃ and PDPA-pSiPh₃

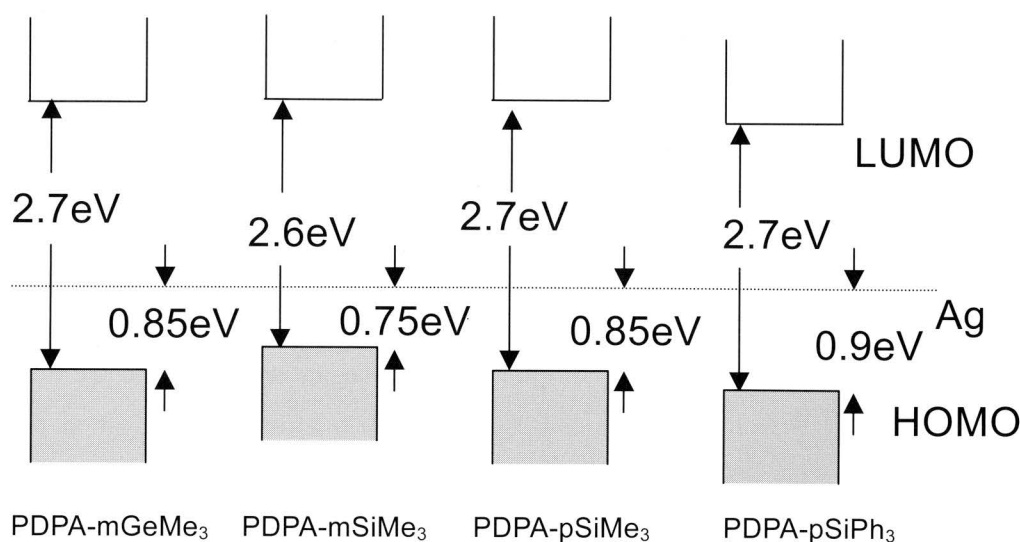


Fig.4:Electronic energy band diagrams of PDPA derivatives.

The position of the substitution also influenced the absorption edge and peak wavelength of PL. As evident in Fig. 3, the absorption edge and a PL peak of para-substituted PDPA-pSiMe₃ are located at shorter wavelength compared with those of meta-substituted PDPA-mSiMe₃. The peak wavelengths of absorption and PL were 422 nm and 523 nm in PDPA-pSiMe₃, respectively.⁸⁾

The origins of these substituted-position effects are not clear at this stage, however, we are speculating as follows. In meta-substituted PDPA, the substituted benzene nuclei may not be in the same plane with the conjugated electron system of the main chain because of the larger steric hindrance effect, but in the case of para-substituted PDPA they may be in co-planar. These effects cause more extensive π electron delocalization on the main chain for the meta-substituent and influence the electronic interaction between the main-chain and the substituent.⁸⁾ That is the conjugation system of the main chain in meta-substituted PDPA

derivatives may be less modified from non-substituent polyacetylene with small bandgap, therefore in meta-substituted PDPA with smaller interaction, the band gap energy might be slightly smaller than para-substituted PDPA, resulting in the red shift as observed in Fig.3.

From the analysis of the absorption spectral edge corresponding to the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of PDPA derivatives and the observed threshold potentials of the electrochemical oxidation in the cyclic voltamogram, the electronic energy diagrams in these polymers were evaluated as shown in Fig. 4. The band gap energy of PDPA-mSiMe₃ was estimated to be smaller than that of PDPA-pSiMe₃ actually.

As shown in Fig. 3, among PDPAs with the same Si containing substituents at para position, strong green emission with slightly higher PL efficiency of 28% (photon/photon) as indicated in

Table.1 was observed in PDPA-pSiPh₃ than that of PDPA-pSiMe₃.

Figure5 shows the PL spectra of PDPA-mSiMe₃, PDPA-pSiMe₃ and PDPA-mGeMe₃ at

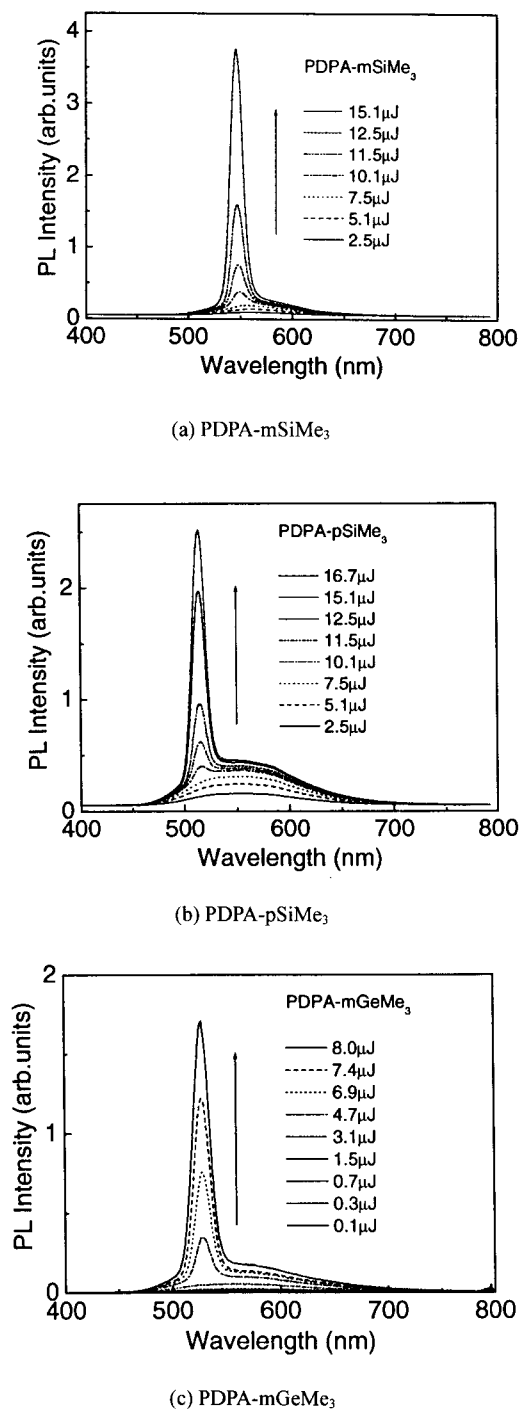


Fig.5:Spectral narrowing in PDPA derivatives

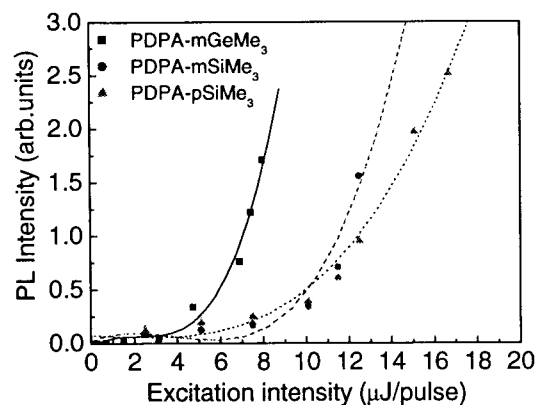


Fig.6:PL intensity at different excitation intensity in PDPA derivatives.

different light excitation intensity. At high excitation light intensity, full width at half maximum (FWHM) of PL spectra became narrow to be about 20 nm in these polymers. But the threshold excitation light intensities of these spectral narrowing were different each other. Figure.6 shows the amplification of PL peak intensity as a function of excitation light intensity. In this figure, the threshold excitation light intensities were about 5 mJ/pulse for PDPA-mGeMe₃ and about 10 mJ/pulse for PDPA-mSiMe₃ and PDPA-pSiMe₃ respectively. These differences should be attributed to electronegativity of hetero-atoms in the substituents or the difference of effective conjugation length.

At this stage, it can be considered that these phenomena can be ascribed to amplified spontaneous emission (ASE). It could be considered that these PDPA has the possibility to the application to green emission organic laser diode.

From time resolved PL measurements, PL decay time at PL peak wavelength could be approximated by double-exponential decay¹⁵:

$I(t) = I_{of} \exp(-t/\tau_f) + I_{os} \exp(-t/\tau_s)$, where $I(t)$ is the PL intensity at time t , I_{of} and I_{os} are the initial intensities, and τ_f and τ_s are the lifetime constants of fast and slow components, respectively. Therefore, the PL decay times of PDPA-mSiMe₃ at peak wavelength were evaluated to be $\tau_f = 67$ ps and $\tau_s = 358$ ps, that were shorter than PDPA-pSiMe₃ as shown in Fig. 7. The difference of the decay time might be due to the longer conjugation of PDPA-mSiMe₃ and due to the strong inter-chain interaction, resulting in the longer diffusion length of photo-excited excitons and nonradiative emission upon encountering the quenching center. Detailed studies are now in progress to clarify the emission mechanism of PDPA derivatives with substituents containing Si and Ge atoms.

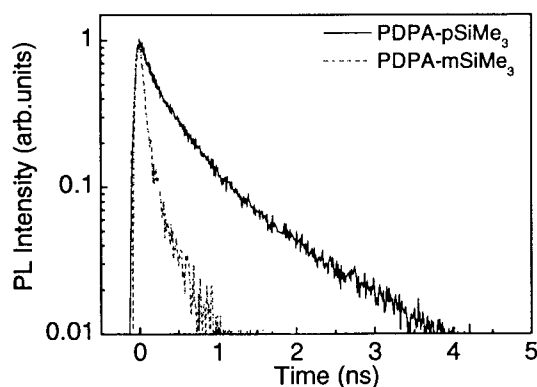


Fig.7: PL decays of PDPA-pSiMe₃ and PDPA-mSiMe₃ in thin films.

In the case of EL diodes utilizing these PDPA derivatives as emission layers, that is, with a structure of ITO/PDPA derivative/MgAg, strong green EL was observed. By applying a positive bias voltage onto ITO anode, a bright green emission was obtained, the EL spectra of which are shown in Fig. 8. The emission peak wavelengths of PDPA derivatives are around 520-540 nm, which almost coincided with

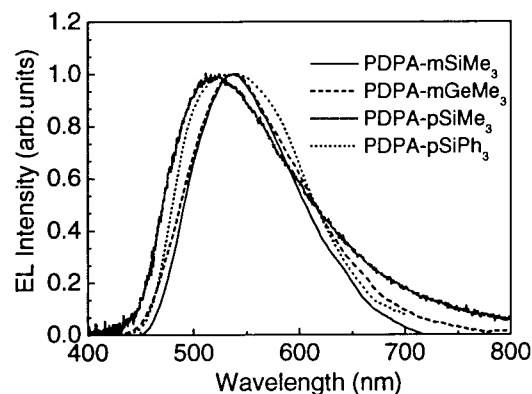


Fig.8: EL spectra of PDPA derivatives.

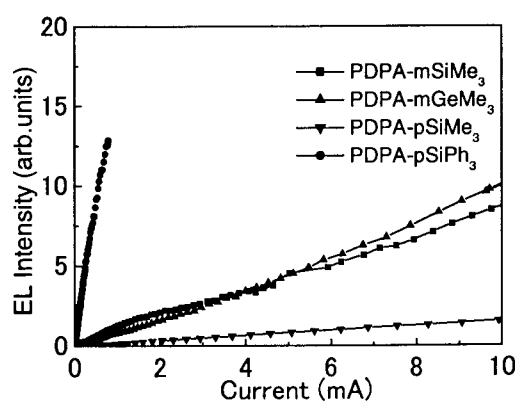


Fig.9: Current-EL intensity characteristics of EL devices with thin films of PDPA derivatives.

those of PL. The EL diodes exhibited typical rectifying characteristics. That is, in this case, ITO and MgAg layers act as hole and electron injecting electrodes, respectively. The turn-on voltage of the EL diodes with PDPA-pSiPh₃ film was slightly higher than the other EL diodes with PDPA derivatives in spite of almost equivalent film thickness. The HOMO level of PDPA-pSiPh₃ is relatively low in comparison with the other PDPA derivatives as shown in Fig. 4, which might relate with the turn-on voltages. The emission intensity increased monotonically with increasing injection current. EL intensity was larger in PDPA-derivatives with more bulky substituents such as PDPA-pSiPh₃, as evident in

Fig.9.

In this figure, comparing EL intensities of PDPA derivatives at the same current, it should be noted that (a) the relative EL efficiency of PDPA-mSiMe₃ is nearly the same with that of PDPA-mGeMe₃, (b) the relative EL efficiency of PDPA-mSiMe₃ is higher than PDPA-pSiMe₃ and (c) the relative EL efficiency of PDPA-pSiPh₃ is much larger than PDPA-pSiMe₃, though all these PDPA derivatives exhibit similar PL efficiency as be indicated in Table I. These results may be due to the difference of the injected positive and negative charge carrier balance among PDPA derivatives. For example, in comparison of PDPA-pSiMe₃ and PDPA-pSiPh₃, the balance of injected positive and negative charge carrier should be better in PDPA-pSiPh₃, due to the lower HOMO in the latter, resulting in the better balance.

4.Summary

Optical properties of PDPA derivatives with substituents containing Si and Ge atoms were studied. These PDPA derivatives exhibited highly efficient PL and PL spectral narrowing at high excitation intensity. The peak wavelength of PL spectra depended on the positions of substitution and the atoms in the substituents. EL diodes with emission layers of PDPA-derivatives were fabricated and strong green emission was observed. PL decay was also confirmed to be dependent on the position of the substituents and the hetero-atoms in the substituents.

5.Acknowledgement

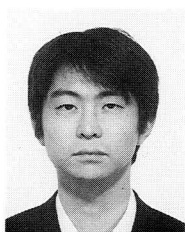
This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Culture, Sports, Science and Technology and from Japan Society for the Promotion of Science.

References

- 1) K. Yoshino, M. Onoda and T. Kawai: Optoelectronics5 (1990)1.
- 2) H. Shirakawa, T. Ito and S. Ikeda: Poly. J. 4(1973)460.
- 3) C. K. Chiang, C. R. Fincher Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau and A. G. MacDiarmid: Phys. Rev. Lett. 39(1977)1098.
- 4) L. Lauchlan, S. Etemad, T. -C. Chung, A. J. Heeger and A. G. MacDiarmid: Phys. Rev. B24, (1981)3701.
- 5) K. Yoshino, S. Hayashi, Y. Inuishi, K. Hattori, and Y. Watanabe: Solid State Commun. 46(1983)583.
- 6) Gontia, S. V. Frolov, M. Liess, E. Ehrenfreund, Z. V. Vardeny, K. Tada, H. Kajii, R. Hidayat, A. Fujii, K. Yoshino, M. Teraguchi and T. Masuda: Phys. Rev. Lett. 82(1999)4058.
- 7) Shukla and S. Mazumdar: Phys. Rev. Lett. 83(1999)3944.
- 8) R. Hidayat, M. Hirohata, K. Tada, M. Teraguchi, T. Masuda and K. Yoshino: Jpn. J. Appl. Phys. 36(1997)3740.
- 9) K. Tada, R. Hidayat, M. Hirohata, M. Teraguchi, T. Masuda and K. Yoshino: Jpn. J. Appl. Phys. 35(1996) L1138.
- 10) M. Hirohata, K. Tada, R. Hidayat, T. Masuda, and K. Yoshino: Jpn. J. Appl. Phys. 36(1997) L302.
- 11) T. Masuda, T. Hamano, K. Tsuchihara, and T. Higashimura: Macromolecules23(1990)1374.
- 12) H. Shirakawa, T. Masuda, and K. Takeda: "The Chemistry of Triple-Bonded Functional Groups", ed. S. Patai (John Wiley & Sons, New York) Chap. 17(1994)945.

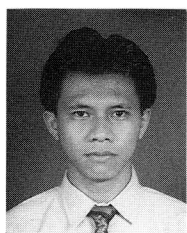
- 13) Y. Ohmori, M. Uchida, K. Muro and K. Yoshino: Jpn. J. Appl. Phys. 30(1991) L1938.
- 14) Y. Ohmori, M. Uchida, K. Muro and K. Yoshino: Jpn. J. Appl. Phys. 30(1991) L1941
- 15) R. Hidayat, S. Tatsuhara, D. W. Kim, M. Ozaki, K. Yoshino, M. Teraguchi and T. Masuda: Phys. Rev. B61(2000)10167

(July 18.2001 accepted)

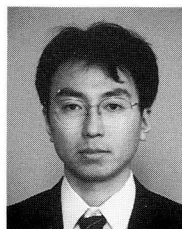


Yusuke Nishihara was born in Ehime, Japan in 1977. He graduated in 2000 from Department of Electrical and Electronic Engineering, Ehime University.

He is now Master course student of Department of Electronic Engineering, Faculty of Engineering, Osaka university and now studying the electronic and optical properties of conducting polymer and application of them to electronic devices such as EL.



Rahamt Hidayat was born in Jakarta, Indonesia in 1969. He graduated in 1998 from Department of Physics, Faculty of Science, Bandung Institute of Technology. He obtained a Doctor of Engineering Degree in 1997 in Osaka University. In that year, he became a research associate in Bandung Institute of Technology.



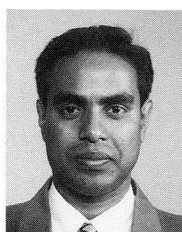
Akihiko Fujii was born in Osaka, Japan in 1969. He graduated in 1993 from Department of Electronic Engineering, Faculty of Engineering, Osaka university,

where he obtained a Doctor of Engineering Degree in 1997. In that year, he became a research fellow of the Japan Society for the Promotion of Science and a visiting scholar of University of Utah in US and he became a research associate, Osaka University in 1998.



Masanori Ozaki was born in Aichi, Japan in 1960. He graduated in 1983 from Department of Electronic Engineering, Faculty of Engineering, Osaka university,

where he obtained a Doctor of Engineering Degree in 1988. In that year, he became a research associate in Osaka University and promoted to Lecturer in 1991. In 1994, he became an Associate Professor, Osaka University.

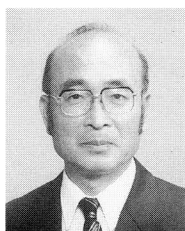


S.M. Abdul Karim was born in Bangladesh. He graduated in 1996 from Department of Materials Science, Toyohashi university of Technology. He is

now doctor course student of Department of Polymer Chemistry, Kyoto university.



Toshio Masuda was born in Japan. He graduated in 1967 from Department of Polymer Chemistry, Kyoto university, where he obtained a Doctor of Chemistry Degree in 1971. In that year, he became an research associate in Kyoto University and promoted to Associate Professor in 1981. In 1993, he became a professor in Department of Polymer Chemistry, Kyoto university.



Katsumi Yoshino was born in Shimane, Japan in 1941. He graduated in 1964 from Department of Electronic Engineering, Faculty of Engineering, Osaka university, where he obtained a Doctor of Engineering Degree in 1969. In that year, he became an Assistant in Electrical Engineering, Osaka University and promoted to Lecturer in 1972, Associate Professor in 1978. In 1988, he became a Professor, Osaka University.