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

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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

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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 state1Bu and2Ag 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 containig a hetero-atom such as silicon (Si) also possessed efficient emission characteristics. The effects of hetro-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 containig 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-(trime thylgermyl) phenylacetylene)(PDPA-mGeMe3),poly(1-phenyl -2-p-(trimethylsilyl)phenylacetylene)(PDPA-pSi Me3),poly(1-phenyl-2-p-(tri-phenylsilyl)phenyla cetylene)(PDPA-pSiPh3),the molecular structures
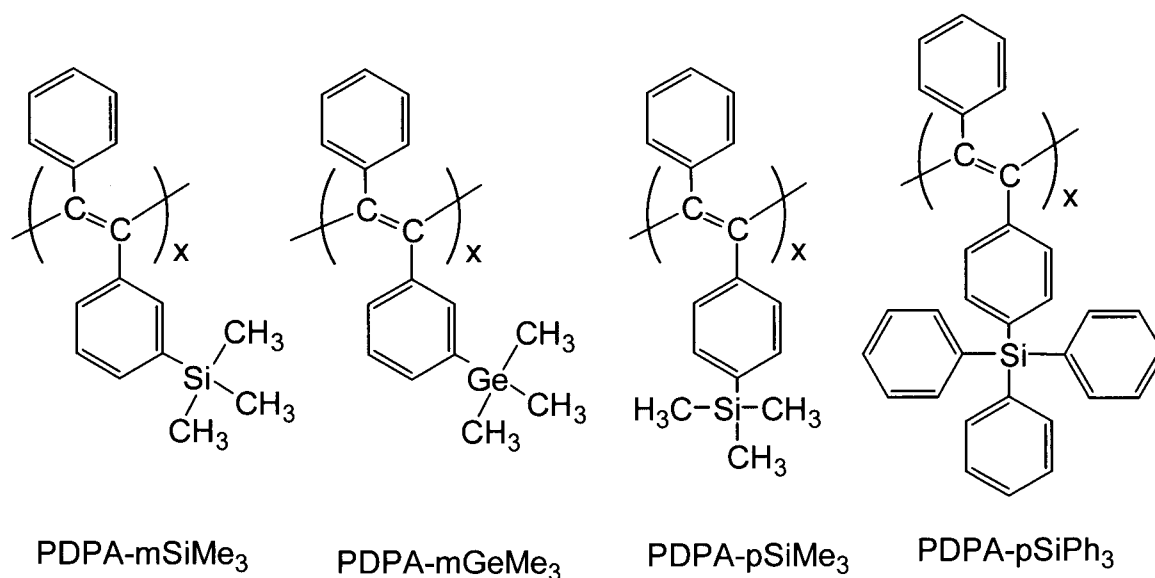
PDPA-mSiMe₃ 　　PDPA-mGeMe₃ 　　PDPA-pSiMe₃ 　　PDPA-pSiPh₃

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-mSiMe₃	434	548	27
PDPA-mGeMe₃	422	540	26
PDPA-pSiMe₃[8,9]	422	523	25
PDPA-pSiPh₃	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 with150ps pulses with the energy per pulse ranging from0.1to20mJ/pulse provided by a Ti:Saphire mode-locked laser, the wavelength of which was400nm. 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-105function generator and the HA-105potentiostat.

EL devices with the structure of indium-tin-oxcide(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 was4mm2. 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 about100fs and pulse rate of82MHz. PL was observed using a streak camera, which determined the resolution of the measurement to be about15ps. This measurement was carried out at room temperature in an evacuated quartz vessel.

3.Results and Discussion

Figure2shows absorption and PL spectra of PDPA-mSiMe3and PDPA-mGeMe3in films. The peak wavelengths of absorption and PL were 434nm and548nm in PDPA- mSiMe3 and 422nm and540nm in PDPA-mGeMe3, respectively. It

should be noted that the absorption edge and the PL peak of PDPA-mSiMe3in film were located at longer wavelength than those of PDPA-mGeMe3. Similar redshifts of absorption edge and PL peak were also observed in PDPA-mGeMe3solution. 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-m SiMe3and PDPA-mGeMe3may have influenced.

Both PLs of PDPA-mSiMe3 and PDPA-m GeMe3were strong green emissions, and the PL efficiency of PDPA-mSiMe3was nearly the same with that of PDPA-mGeMe3,26-27% (photon /photon), as summarized in Table I.
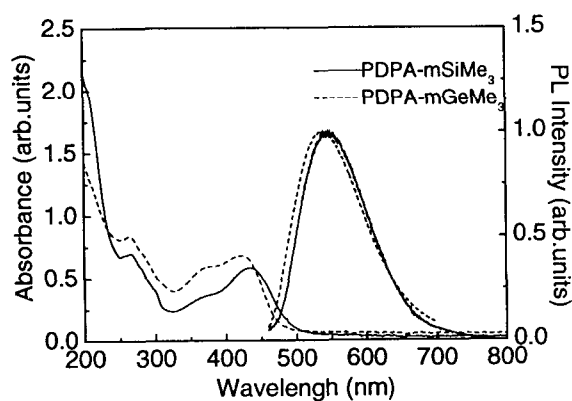

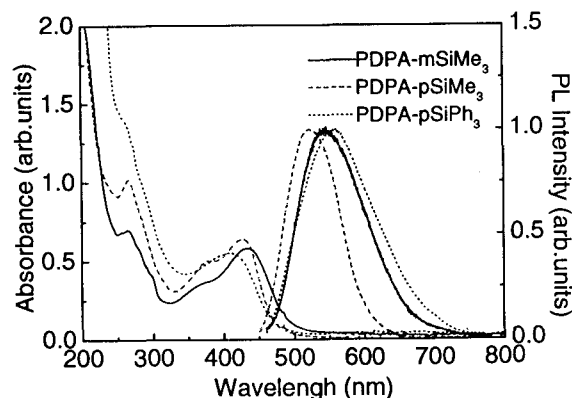Fig.2:Absorption and PL spectra of PDPA-mSiMe₃ and PDPA-mGeMe₃

Fig.3:Absorption and PL spectra of PDPA-mSiMe₃, PDPA-pSiMe₃ and PDPA-pSiPh₃
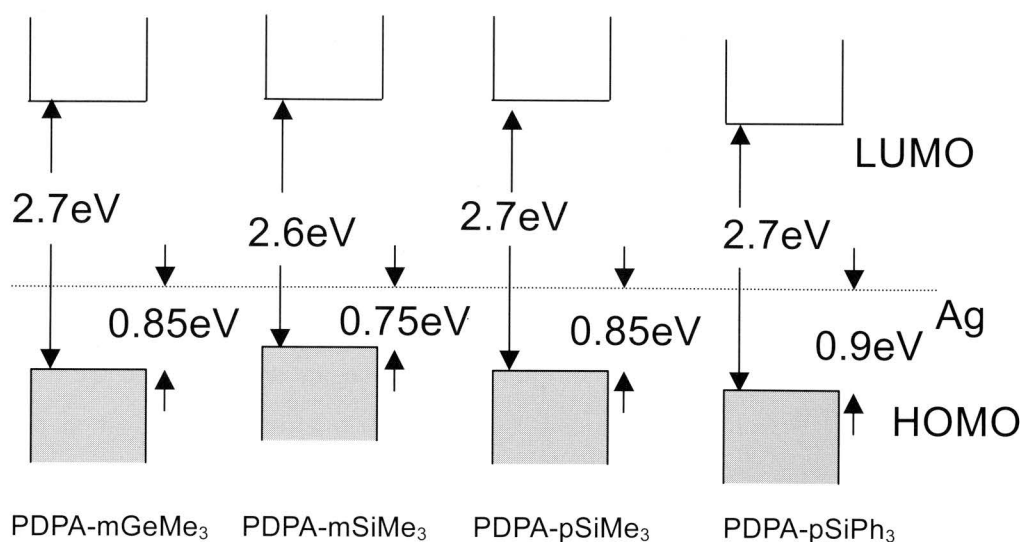
Fig.4:Electronic energy band diagrams of PDPA derivatives.

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 523nm 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-mSiMe3was 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.1was observed in PDPA-pSiPh₃ than that of PDPA-pSiMe₃.

Figure5 shows the PL spectra of PDPA-m SiMe₃, PDPA-pSiMe₃ and PDPA-mGeMe₃ at
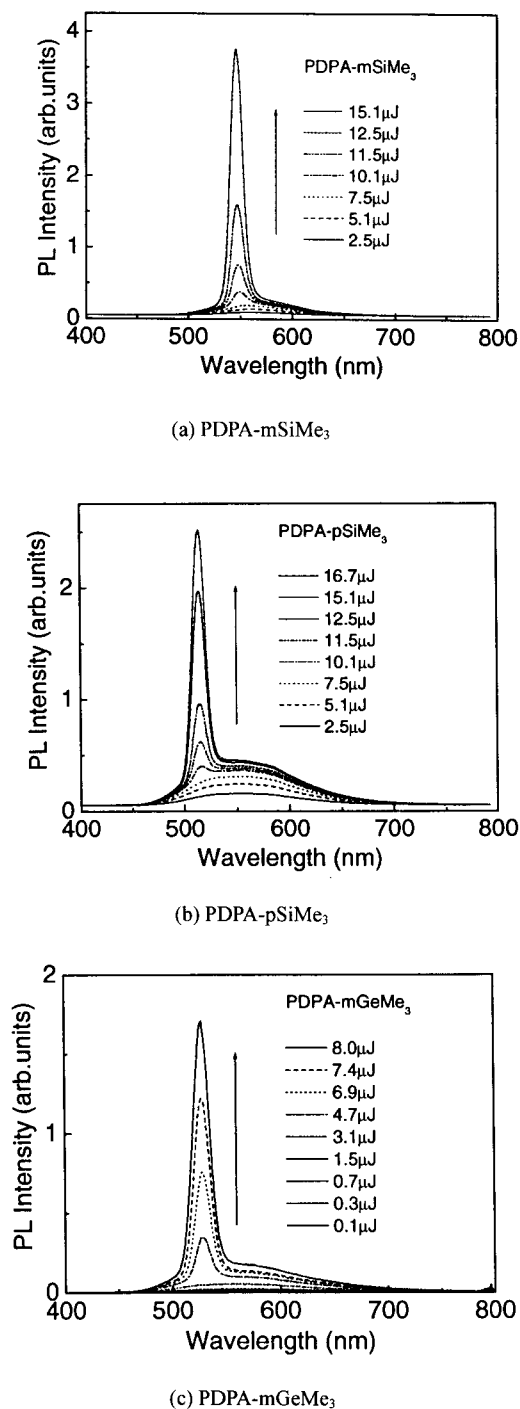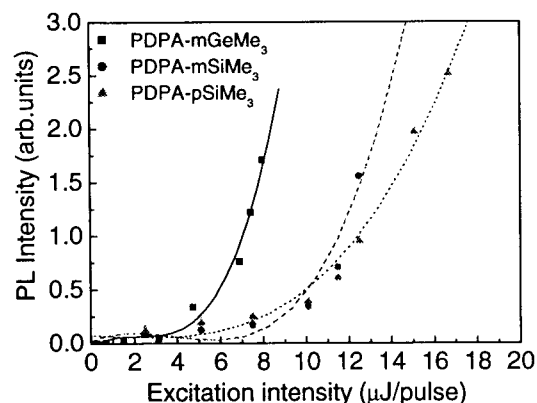

Fig.6:PL intensity at different excitation intensity in PDPA derivatives.

different light excitation intensity . At high excitation light intensity, full width at half maximum (FWHM) of PL spectra became narrow to be about20nm in these polymers. But the threshold excitation light intensities of these spectral narrowing were different each other. Figure.6shows the amplification of PL peak intensity as a function of excitation light intensity.In this figure, the threshold excitation light intensities were about5 mJ/pulse for PDPA-mGeMe₃ and about10mJ/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):

(a) PDPA-mSiMe₃

(b) PDPA-pSiMe₃

(c) PDPA-mGeMe₃

Fig.5:Spectral narrowing in PDPA derivatives

I(t)=Iofexp(-t/ τ f)+Iosexp(-t/ τ s), where I(t) is the PL intensity at time t, Iof and Ios 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-mSiMe$_3$ at peak wavelength were evaluated to be τ f=67ps and τ s=358ps, that were shorter than PDPA-pSiMe$_3$ as shown in Fig. 7. The difference of the decay time might be due to the longer conjugation of PDPA-mSiMe$_3$ 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.
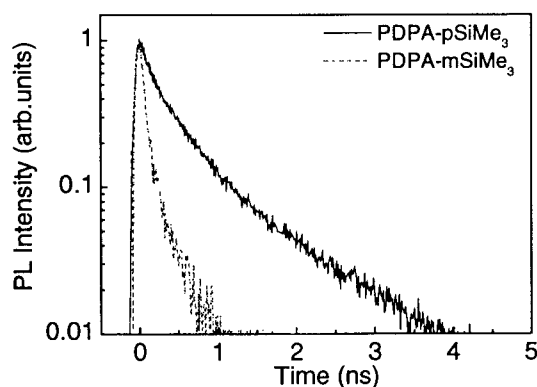

Fig.8:EL spectra of PDPA derivatives.

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

Fig.7:PL decays of PDPA-pSiMe$_3$ and PDPA-mSiMe$_3$ 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 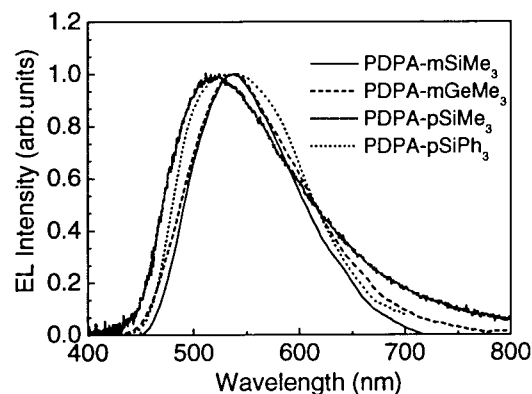derivatives are around520-540nm, which almost coincided with those of PL. The EL diodes exhibited ty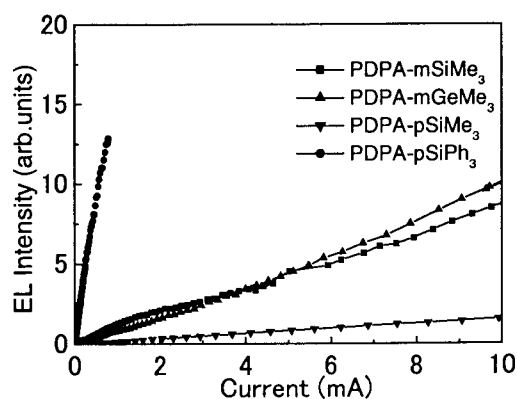pical rectifying characteristics. That is, in this case, ITO and MgAg layers act as hole and electron injecting electrodes, respectively. The turn-on voltage of the EL diodes with PDPA-pSiPh$_3$ film was silightly higher than the other EL diodes with PDPA derivatives in spite of almost equivalent film thickness . The HOMO level of PDPA-pSiPh$_3$ 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-pSiPh$_3$, 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-mSiMe$_3$ is nearly the same with that of PDPA-mGeMe$_3$, (b) the relative EL efficiency of PDPA-mSiMe$_3$ is higher than PDPA-pSiMe$_3$ and (c) the relative EL efficiency of PDPA-pSiPh$_3$ is much larger than PDPA-pSiMe$_3$, 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-pSiMe$_3$ and PDPA-pSiPh$_3$, the balance of injected positive and negative charge carrier should be better in PDPA-pSiPh$_3$, 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

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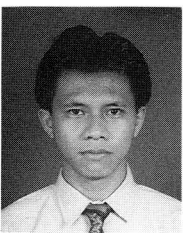
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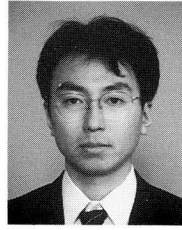
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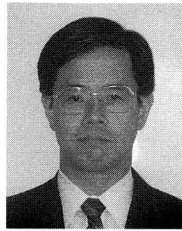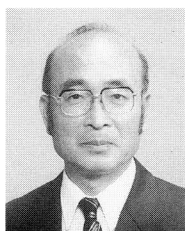
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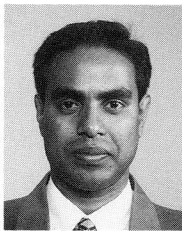
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