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Optical Properties of Star-Like Branched Organosilicon Compounds

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Optical absorption and photoluminescence (PL) spectra, time-resolved PL and electroluminescence (EL) in star-like branched organosilicon compounds have been found to be dependent on the length and number of oligothiophylene units in each arm. Films of the organosilicon compounds with two oligothiophylene unit in each arm have been found to exhibit two PL peaks but a single peak in those with one oligothiophylene unit. Origin of the PL peaks is discussed in terms of the disorder in films and localized state related to the disorders in the film.

KEYWORDS : organosilicon compounds, oligothiophylene, photoluminescence, electroluminescence,
X-ray diffraction, silanylene

星状分岐型有機シリコン化合物の光学的性質

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星状分岐型有機シリコン化合物の光学吸収、蛍光(PL)、時間分解PL、電界発光(EL)において、分子中のオリゴチエニレンの長さや数についての依存性を明らかにした。オリゴチエニレンユニットが二つある場合、PLピークが二つ存在し、オリゴチエニレンユニットが一つの場合PLピークは一つである。PLピークについては、フィルム中の欠陥や欠陥による局在状態により発現すると考えられる。

1. Introduction

Conducting polymers with highly extended π -electron systems in their main chains have attracted much interest from both fundamental and practical view points, because of their novel physical phenomena such as an insulator-metal transition upon doping and various new functional applications such as battery, electrochromism, electroluminescence (EL) devices and high efficiency of photovoltaic device.¹⁻³⁾

On the other hand, polysilanes, which are considered to be one-dimensional systems with conjugation of σ -electrons along the Si backbone, have also attracted much attention, because of various interesting phenomena such as doping effects, thermochromism and photoconductive response with large hole mobility.^{4,5)} We have also reported that PL is quenched upon C_{60} doping in polysilanes with aromatic moieties in the side chain.⁶⁾ EL was also reported in polysilanes.^{7,8)}

Therefore, molecules, oligomers and polymers containing silanylene and aromatic molecules with π -conjugated electron systems in their main chains are interesting from both scientific and practical points of view. Recently, we have reported the unique properties of poly(disilanyleneoligophenylene)s, the backbone main chain structure of which consists of disilanylene and oligophenylene units.^{9,10)}

Poly(disilanyleneoligothienylene) with disilanylene and oligothienylene in the main chain also exhibited novel characteristics. Intense EL was also observed in these polymers.¹¹⁾

In EL devices utilizing low molecular weight of organic molecules as a light emissive layer or a carrier transporting layer, non-planar molecules such as star-shaped molecules are found to exhibit stable EL characteristics, perhaps due to the stability of the amorphous state of these molecules in films because of high glass transition temperature, which stimulated much interest in new stable non-planar molecules in

films.

In this paper, we report the unique optical properties such as PL and EL in newly developed branched organosilicon compounds molecules depending on the length and number of oligoethienylene units in each arm.

2. Experimental

Figure 1 indicates molecular structures of star-like branched organosilicon compounds used in this study and their abbreviated names. These star-like branched structures of organosilicon compounds were prepared by the nucleophilic substitution reaction of lithiooligothiophenyl derivatives with tris (chlorodimethylsilyl)-methylsilane. Detailed preparation method and procedure of the branched organosilicon compounds and their chemical and structural analysis were reported in the previous paper.¹²⁾

These star-like organosilicon compounds are soluble in common solvents such as chloroform and toluene. Films of these molecules were prepared on quartz plates and In-Sn-oxide (ITO) coated quartz plates by spin-coating of the chloroform or toluene solution.

Optical absorption and photoluminescence (PL) spectra were measured with a Hewlett Packard 8452A spectrophotometer and a Hitachi F-2000 fluorescence spectrophotometer, respectively.

Time-resolved PL measurements were carried out using a femto-second (fs) laser system. A diode pumped laser (Millenia, Spectra Physics) beam was passed through a Ti-Sapphire mode-locked laser (Tsunami, Spectra Physics) to obtain laser pulse of 80 fs with pulse trains of 82 MHz and then frequency doubled to 398 nm by a second harmonic generator unit utilizing barium beta borate crystals (Frequency Doubler 3985, Spectra Physics). The PL decay and time-resolved PL spectra were measured at the same time using a streak scope camera (Streak Scope

C4334, Hamamatsu). The time resolution of this experiment was about 10 ps.

X-ray diffraction was studied utilizing a RINT 1100 (RIGAKU) system with X-ray of 1.54 Å in wavelength.

Electroluminescence (EL) was studied utilizing devices with the structure of MgIn/organosilicon compound/ITO using the conventional method previously reported by us.^{13,14)}

3. Results and Discussion

Figure 2 (a) and (b) show absorption spectra of five organosilicon compounds in chloroform solutions and in films, respectively. As evident in these figures both in solutions and in films organosilicon compounds containing terthienylene (TTT) units in arms such as $\text{SiMe}(\text{SiMe}_2\text{TTEt})_3$, $\text{SiMe}(\text{SiMe}_2\text{TTSiMe}_3)_3$ and $\text{SiMe}(\text{SiMe}_2\text{TTSi}(\text{iPr}_2)\text{Si}(\text{iPr}_2)\text{TTEt})_3$ exhibit peaks at longer wavelength than those containing bithienylene (TT) units in the arm such as $\text{SiMe}(\text{SiMe}_2\text{TTBr})_3$ and $\text{SiMe}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TT})_3$ by about 40 nm. This indicates that the absorption in the visible range may be mainly originated in the absorption of oligothiénylene just as the case of linear oligosilanylène oligothiénylene polymers.⁹⁾

Figure 3 (a) and (b) show PL spectra of five star-like branched organosilicon compounds in chloroform solutions and in films, respectively. It is also evident in these figures that in solutions the organosilicon compounds containing terthienylene in the arms such as $\text{SiMe}(\text{SiMe}_2\text{TTEt})_3$, $\text{SiMe}(\text{SiMe}_2\text{TTSiMe}_3)_3$ and $\text{SiMe}(\text{SiMe}_2\text{TTSi}(\text{iPr}_2)\text{Si}(\text{iPr}_2)\text{TTEt})_3$ indicate a PL peak at longer wavelength compared with those containing bithienylene in the arm such as $\text{SiMe}(\text{SiMe}_2\text{TTBr})_3$ and $\text{SiMe}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TT})_3$. This is also reasonable because the optical property of these samples in the visible range mostly originates in those of oligothiénylene.

Similar PL peaks were also observed in the films of organosilicon compounds at similar wavelength with those in solutions. Also organosilicon compounds containing terthienylene in the arm exhibited red shift of PL compared with those containing bithienylene in the arm.

However, it should be noted that in the films of organosilicon compounds with two or three oligothiénylene units in each arm such as $\text{SiMe}(\text{SiMe}_2\text{TTSi}(\text{iPr}_2)\text{Si}(\text{iPr}_2)\text{TTEt})_3$ and $\text{SiMe}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TT})_3$ the second peak was observed at longer wavelength contrary to organosilicon compounds with a single oligothiénylene unit in each arm in which only single

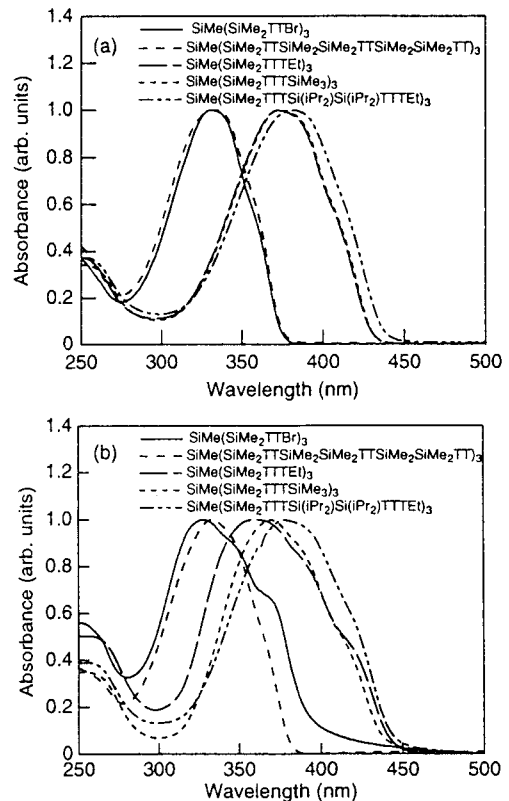


Fig. 2. Absorption spectra of organosilicon compounds (a) in chloroform solutions and (b) in films.

図2.有機シリコン化合物の吸収スペクトル(a)クロロホルム溶液(b)薄膜

PL peak was observed even in the film.

The origin of this second peak seems not to be due to the phonon side band, because such second peak was not observed in the solution. That is, the existence of the second peak is not an intrinsic property characteristic to the molecular structure itself. Therefore, the second PL peak may be originated in the solid effect. Some defect states may be formed in the film and may be related with the evolution of this PL peak. It should be pointed out that in the compound with only one oligothiophene unit in each arm such a second peak was not observed. In the compound with two or more oligothiophene units in each arm such as $\text{SiMe}(\text{SiMe}_2\text{TTSi}(\text{iPr}_2)\text{Si}(\text{iPr}_2)\text{TTTEt})_3$

$(\text{iPr}_2)\text{TTEt})_3$ and $\text{SiMe}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TT})_3$, the disorder may have stronger effect on PL. That is, star shaped molecular structure with long arms containing many oligothiophenylenes may hinder the formation of good crystalline structure and result in the formation of defect states.

Indeed in organosilicon compounds with two or three oligothiophene units in the side arms we can not observe clear X-ray diffraction peak even by the heat-treatment as shown in Fig. 4. That is, as evident in Fig. 4, $\text{SiMe}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TT})_3$ which was at first heated up to 140 °C and then slowly cooled down to room temperature did not exhibit a clear diffraction peak. On the contrary, in organosilicon compounds with only one oligothiophene unit in each arm for example in $\text{SiMe}(\text{SiMe}_2\text{TTTEt})_3$ clear X-ray diffraction peak evolved with the heat-treatment and subsequent cooling as also indicated in this figure. These observations clearly suggest that the crystallization was strongly hindered in the star-like

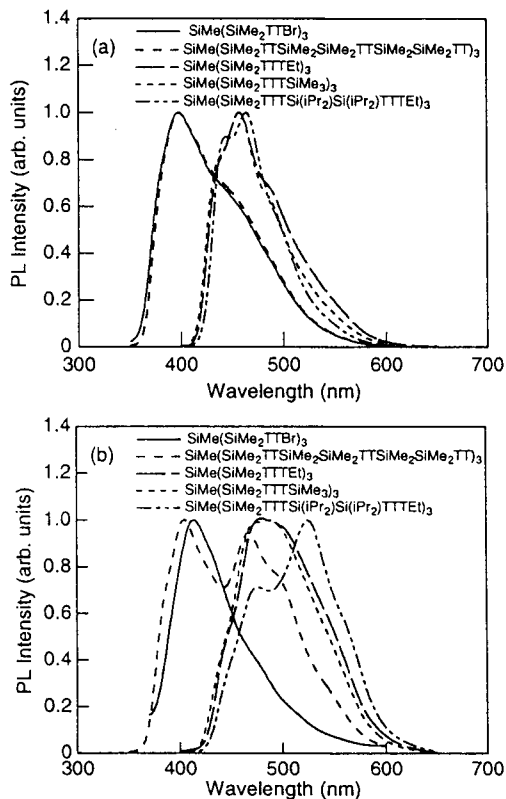


Fig. 3. PL spectra of organosilicon compounds (a) in chloroform solutions and (b) in films.

図3.有機シリコン化合物のPLスペクトル(a)クロロホルム溶液(b)薄膜

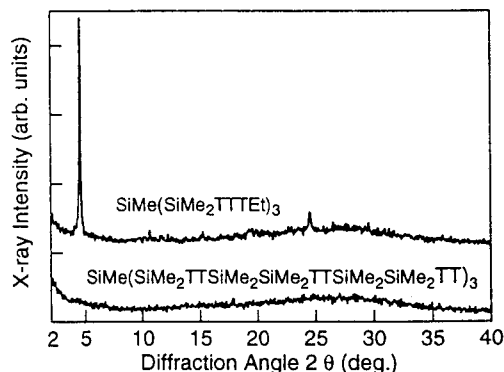


Fig. 4. X-ray diffraction patterns of $\text{SiMe}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TT})_3$ and $\text{SiMe}(\text{SiMe}_2\text{TTTEt})_3$ after annealing from 140 °C under vacuum.

図4. 真空中140 °C熱処理後の $\text{SiMe}(\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TTSiMe}_2\text{SiMe}_2\text{TT})_3$ と $\text{SiMe}(\text{SiMe}_2\text{TTTEt})_3$ のX線回折パターン

branched organosilicon compounds with plural oligothiophylene units in each arm.

For further confirmation of this interpretation, we have carried out a time-resolved spectroscopy. If the second peak was just the phonon-side band, the decay kinetics of both peaks in PL should be the same. However, as shown in the inset of Fig. 5, the decay time of the first peak at the shorter wavelength was much shorter than that of the second peak. That is, this can be interpreted by the energy transfer from the higher energy excitons corresponding to the first peak to the lower energy trapped state contributing

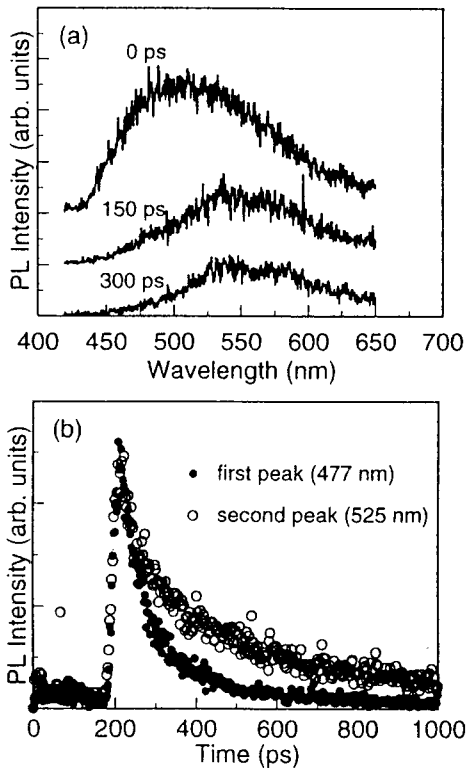


Fig. 5. Time-resolved PL spectra of SiMe(SiMe₂TTTSi(iPr₂)Si(iPr₂)TTTEt)₃ (a) and time decay curves of PL intensity of two peaks (b).

図5 .SiMe(SiMe₂TTTSi(iPr₂)Si(iPr₂)TTTEt)₃の時間分解PLスペクトル(a)及び二つのPLピークの時間減衰曲線(b)

to the second peak. This situation was more clearly indicated in the time-resolved PL spectra shown in Fig. 5. That is, the first peak appears just after the optical excitation and then accompanying with the decay of the first peak the second peak evolves as time lags in consistent with the above interpretation.

Figure 6 shows the EL spectra observed in the device with the structure of MgIn/organosilicon compound/ITO. Clear green emission was observed in this device upon application of negative voltage to the MgIn electrode. This is typical EL characteristics similar to conducting polymer EL devices. That is, EL emission is interpreted to be originated by the radiative recombination of exciton at the oligothiophylene unit in the arm of the organosilicon compound formed by encountered electrons injected from MgIn cathode and holes injected from ITO anode. However, the threshold voltage of EL emission is slightly higher than 10 V.

Generally polymers and molecules containing Si-Si bonds in the main chain is considered to be relatively unstable. However, the star-like branched organosilicon compound was confirmed to be stable.

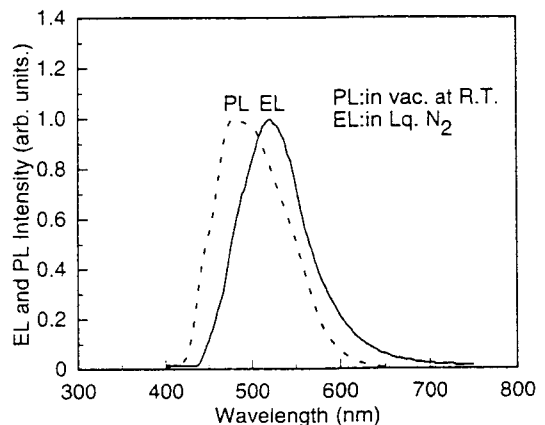


Fig. 6. EL spectrum of MgIn/SiMe(SiMe₂TTTEt)₃/ITO (solid line) and PL spectrum (dashed line).

図6 .MgIn/SiMe(SiMe₂TTTEt)₃/ITOのELスペクトル(実線)とPLスペクトル(破線)

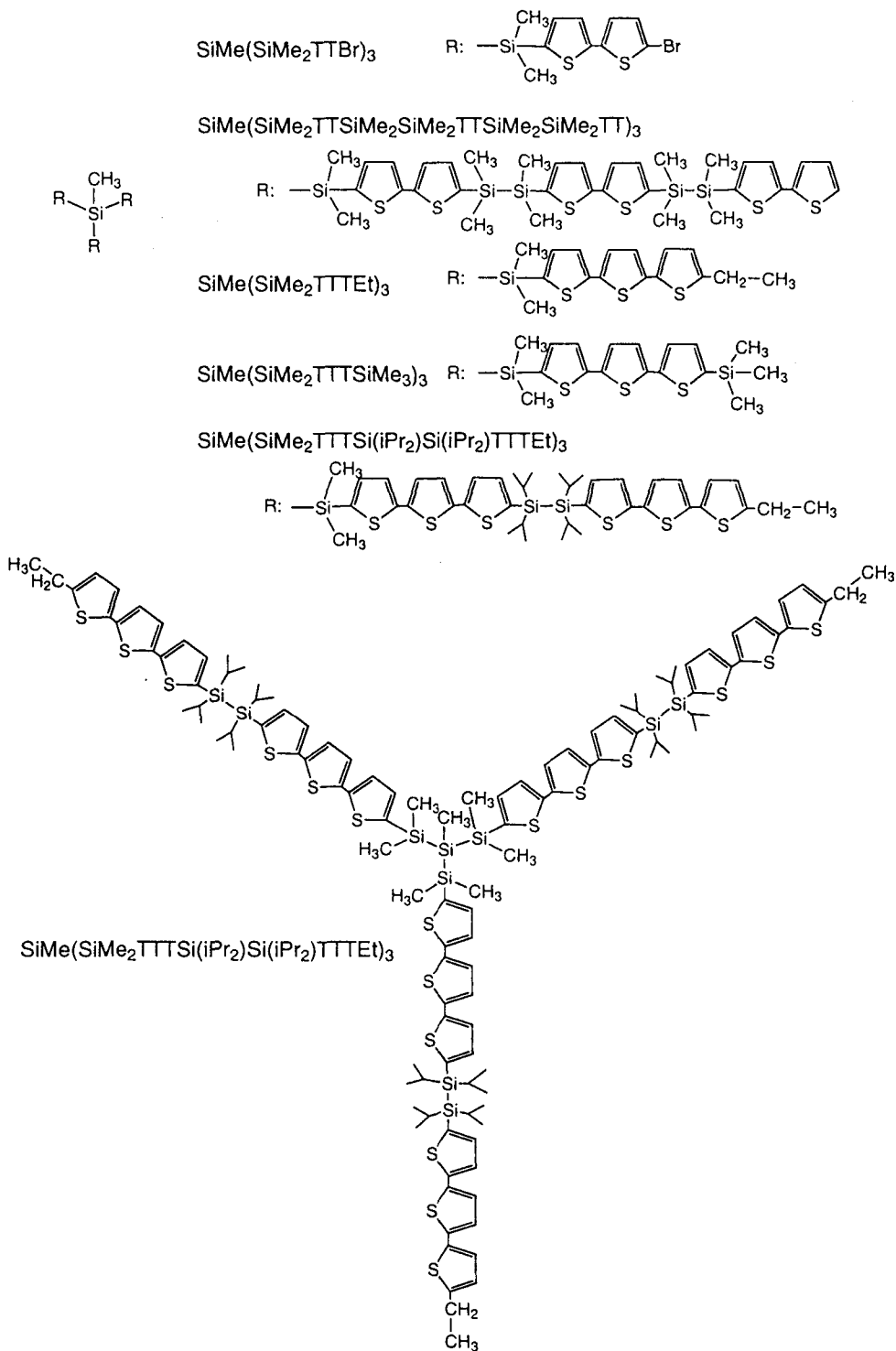


Fig. 1. Molecular structures of star-like branched organosilicon compounds.

図 1 . 星状分岐型有機シリコン化合物の分子構造

Detailed study on the stability has been explained elsewhere.¹⁵⁾

4. Summary

The present experimental study can be summarized as follows.

- (1) Star-like branched structures of organosilicon compounds were prepared and their optical properties were found to be dependent on the sort and number of oligothiénylene unit in each arm.
- (2) Organosilicon compounds containing terthiénylene units in the arm exhibited red shift in absorption and fluorescence in comparison with those containing bithiénylene units.
- (3) In the films of star-like branched organosilicon compounds with plural oligothiénylene units in each arms, two PL peaks were observed. The origin of the second peak at the longer wavelength was interpreted in terms of not a phonon side band but of difficulty in crystalline formation of such compounds.
- (4) The time-resolved PL spectroscopy in the compounds with two PL peaks indicated that the second PL peak at the longer wavelength is not the phonon side band of the first peak and the energy transfer from the excited state corresponding to the first peak to the trapped state corresponding to the second peak plays role, supporting the interpretation in (3).
- (5) Stable amorphous state was confirmed in the organosilicon compound containing plural oligothiénylene units in the side chain.
- (6) Green EL was observed in the device of MgIn/organosilicon compound/ITO structure.

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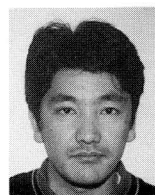
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