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# Solid State Photoluminescence Property of a Novel POSS-Based Material Having Carbazole

*Ichiro Imae,*[1,2] Yusuke Kawakami,[2] Yousuke Ooyama,[1] Yutaka Harima[1]*

**Summary:** Octakis[2-carbazol-9-yl]ethyldimethylsiloxy]silsesquioxane (**POSS-Cz**) was newly synthesized and its photoluminescence properties in both solution and solid states were investigated. **POSS-Cz** showed monomeric emission peak not only in solution state but also in solid state. This result suggests that the introduction of octasilsesquioxane core will suppress the aggregation of carbazole even in solid state.

**Keywords:** amorphous; luminescence; morphology; oligomers; silsesquioxane

## Introduction

Polyhedral oligomeric silsesquioxanes (POSSs) are well-known as novel building blocks for inorganic-organic hybrid materials.[1] POSSs can have an organic substituents on each silicon atom at the corner of the core, which is directed radially, and their core is based on insulating siloxane bond. Thus, when photo- and electroactive chromophores are introduced as the organic substitutents on silicon atom, these chromophores are expected to be isolated from each other by both steric and electronic effects. The isolation of the chromophores will solve the problems due to their aggregation in solid state caused by π-π interactions, such as crystallization and formation of excimers. However, there are few reports on the introduction of photo- and electroactive chromophores as the substitutent on silicon atom of POSS.

We report here on the synthesis of perfectly substituted POSS having carbazole as a photo- and electroactive chromophore, and on its morphological and photoluminescence properties in solid state.

## Experimental Part

### Synthesis of Octakis[2-(carbazol-9-yl) ethyldimethylsiloxy]silsesquioxane (POSS-Cz)

To a solution of octakis(dimethylsiloxy)silsesquioxane 0.92 g (0.9 mmol) and 9-vinylcarbazole 1.96 g (10 mmol) in dry toluene (10mL) was added a solution of platinum-divinyltetramethyldisiloxane complex in xylene (2% Pt, 50 μL). After being stirred until the signal ascribed to Si–H in $^1$H NMR spectrum was disappeared, the solvent of the mixture was evaporated, and resulting viscous brown-colored liquid was purified by reprecipitation from toluene solution (6 mL) to *n*-hexane (120 mL) to give white solid. Then, the white solid was further purified by silica-gel column chromatography (Wakogel C-300, eluent = toluene/*n*-hexane (2/1)) and preparative size-exclusion chromatography (Shodex KF-2001 and KF-2002, eluent = THF). Finally, the product was purified by reprecipitation again to give 1.85 g of white powder (70% yield).

$^1$H NMR (500 MHz, CDCl$_3$): δ 0.02 (s, C$\boldsymbol{H}_3$, 48H), 1.04 (t with fine coupling, SiC$\boldsymbol{H}_2$, 16H, $J = 8.47$, 3.43 Hz), 4.18 (t with fine coupling, CzC$\boldsymbol{H}_2$, 16H, $J = 8.47$, 3.43 Hz), 7.09 (t, $\boldsymbol{H}^c$, 16H, $J = 7.09$ Hz), 7.15 (d, $\boldsymbol{H}^a$, 16H, $J = 7.09$ Hz), 7.29 (t, $\boldsymbol{H}^b$, 16H, $J = 7.09$ Hz), 7.98 (d, $\boldsymbol{H}^d$, 16H, $J = 7.09$ Hz). $^{13}$C NMR (125 MHz, CDCl$_3$): δ −0.25 ($\boldsymbol{C}$H$_3$), 17.84 (Si$\boldsymbol{C}$H$_2$), 37.66 (Cz$\boldsymbol{C}$H$_2$), 108.34 ($\boldsymbol{C}^b$), 118.69 ($\boldsymbol{C}^d$), 120.34

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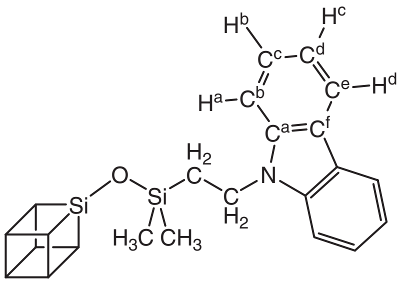
[1] Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan
Fax: (+81)82-424-7688
E-mail: imae@hiroshima-u.ac.jp

[2] Graduate School of Materials Science, Japan Advanced Institute of Science and Technology [JAIST], 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

($\boldsymbol{C}^e$), 123.02 ($\boldsymbol{C}^f$), 125.49 ($\boldsymbol{C}^c$), 139.64 ($\boldsymbol{C}^a$). $^{29}$Si NMR (99MHz, $CDCl_3$): δ −108.88 (POSS-***Si***), 12.04 (O***Si***$Me_2$). IR (KBr, cm$^{-1}$): 3056, 3022, 2954, 2923, 2898, 2891, 1628, 1597, 1485, 1466, 1452, 1387, 1341, 1334, 1326, 1257, 1237, 1190, 1174, 1152, 1089, 1000, 946, 849, 829, 798, 774, 747, 721, 593, 553. MALDI-TOF MS (m/e) 2564.63 ($M^+$).



### Apparatus

NMR ($^1$H, 500MHz; $^{13}$C, 125.5MHz; $^{29}$Si, 99.5MHz) spectra were obtained in $CDCl_3$ on a Varian Unity *INOVA*. Chemical shifts are reported in ppm relative to internal $CHCl_3$ (7.26, $^1$H), $CDCl_3$ (77.00, $^{13}$C), and internal tetramethylsilane (0.00, $^{29}$Si). MALDI-TOF mass-spectroscopy was carried out by a Model Voyager DERP (PerSeptive Biosystems) with 337nm $N_2$ laser (class 3b). Thermal properties were investigated by differential scanning calorimetry (Seiko Instruments Inc., EXSTAR6000, DSC6200, heating and cooling rate: 10 degree min$^{-1}$) and thermogravimetry (Seiko Instruments Inc., EXSTAR6000, TG/DTA220, heating rate: 5 degree min$^{-1}$). Infrared absorption, electronic absorption and photoluminescence spectra were measured in air with VALOR-III spectrophotometer (JASCO), V-570 spectrophotometer (JASCO), and FP-6500 spectrofluorometer (JASCO), respectively. Quantum yield of solid-state photoluminescence of materials was estimated by C9920-01 absolute PL quantum yield measurement system (Hamamatsu).

## Results and Discussion

### Synthesis of POSS-Cz with Perfectly Uniform Structure

Carbazole was introduced by hydrosilylation reaction between octakis(dimethylsiloxy)silsesquixane and 9-vinylcarbazole in the presence of platinum-divinyltetramethyldisiloxane as a catalyst. The product can be dissolved in common organic solvents, such as toluene, THF, chloroform, dichloromethane, and could be purified by ordinary method, and was characterized by $^1$H, $^{13}$C, $^{29}$Si NMR (Figure 1), and MALDI-TOF MS spectroscopies. These results suggest that the product has perfectly uniform structure without any isomers and structural defects. Very recently, He *et al.* and Laine *et al.* reported on the introduction of oligophenylenes and triarylamines into POSS by Grignard reaction and Heck reaction, respectively, but the position and number of substitutents of these chromophores are not controlled at all.[2] Also, after our preliminary report,[3] Shim *et al.* and Hsu *et al.* succeeded in the introduction of some photo- and electroactive chromophores by the same catalyst.[4]

### Morphology

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were investigated. TGA suggested that **POSS-Cz** is stable until around 400 °C and 450 °C in air and $N_2$, respectively (Figure 2). Compared with poly(9-vinylcarbazole) (**PVCz**), **POSS-Cz** was found to have higher thermal stability. DSC curves of **POSS-Cz** in first and second heating processes are shown in Figure 3. When **POSS-Cz** was heated, it showed only a sharp endothermic peak at 166 °C due to melting. On the other hand, when the sample obtained by cooling the melt sample to 0 °C was heated, it showed only a glass-transition temperature at 37 °C. To understand the morphology of the glassy sample, X-ray diffraction (XRD) and polarized optical microscopic (POM) analyses were carried out. While crystalline

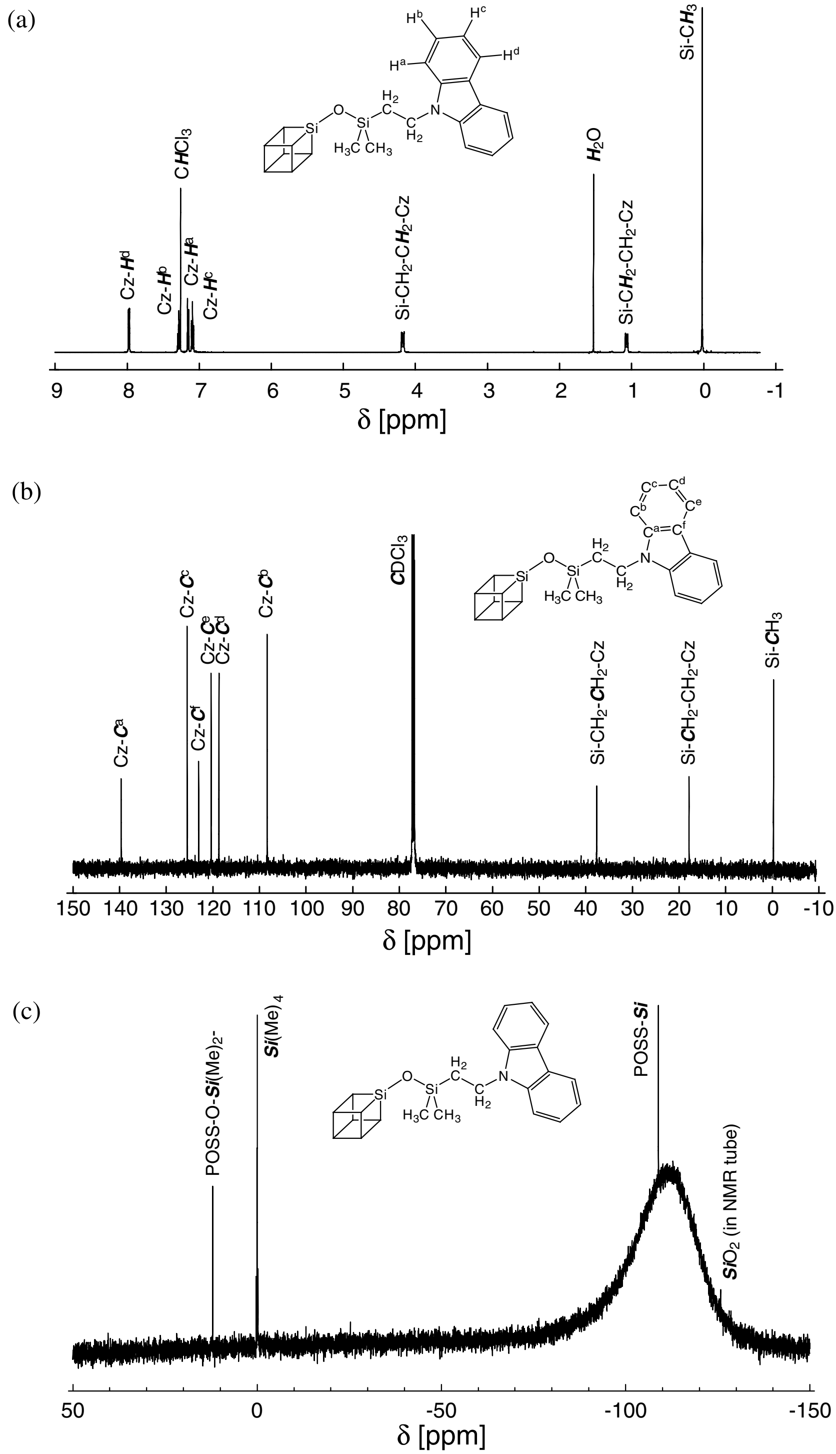
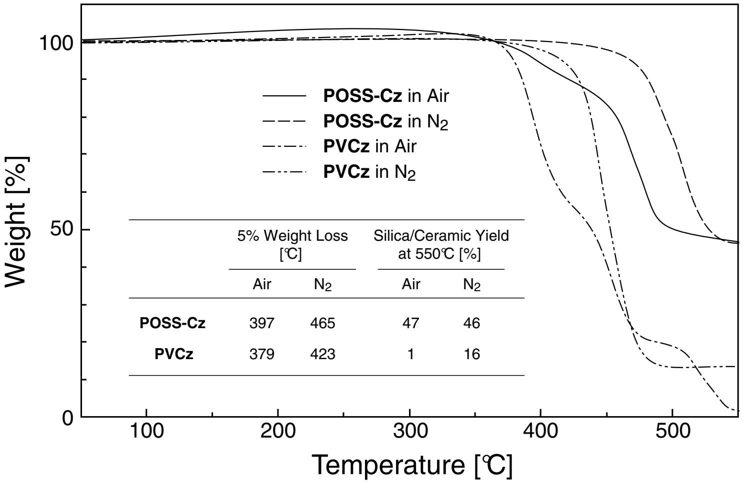


***Figure 1.***
$^{1}$H (a), $^{13}$C (b), and $^{29}$Si (c) NMR spectra of **POSS-Cz**.



| | 5% Weight Loss [℃] | | Silica/Ceramic Yield at 550℃ [%] | |
|---|---|---|---|---|
| | Air | $N_2$ | Air | $N_2$ |
| **POSS-Cz** | 397 | 465 | 47 | 46 |
| **PVCz** | 379 | 423 | 1 | 16 |

*Figure 2.*
TGA curves of **POSS-Cz** and **PVCz**.

**POSS-Cz** showed many sharp peaks in XRD pattern, glassy **POSS-Cz** showed broad hallo. POM image of **POSS-Cz** in cross-nicol state was dark, suggesting it to be isotropic. These results suggest that the glassy **POSS-Cz** is amorphous.

### Photoluminescence

Photoluminescence spectra of **POSS-Cz**, 9-ethylcarbazole (**EtCz**), and **PVCz** in dilute solution ($1 \times 10^{-6}$ mol dm$^{-3}$ in THF) are shown in Figure 4. The spectrum of **POSS-Cz** showed two peaks at 353 and 370nm, which is similar to that of **EtCz**. The quantum yield of **POSS-Cz** in air was estimated by referring to that of *p*-terphenyl ($\phi_{p\text{-terphenyl}} = 0.87$), to be $\phi_{\text{POSS-Cz}} = 0.27$, which is almost the same as that of **EtCz** ($\phi_{\text{EtCz}} = 0.30$). On the other hand, **PVCz** showed weak and broad peak with lower quantum yield ($\phi_{\text{PVCz}} = 0.10$)

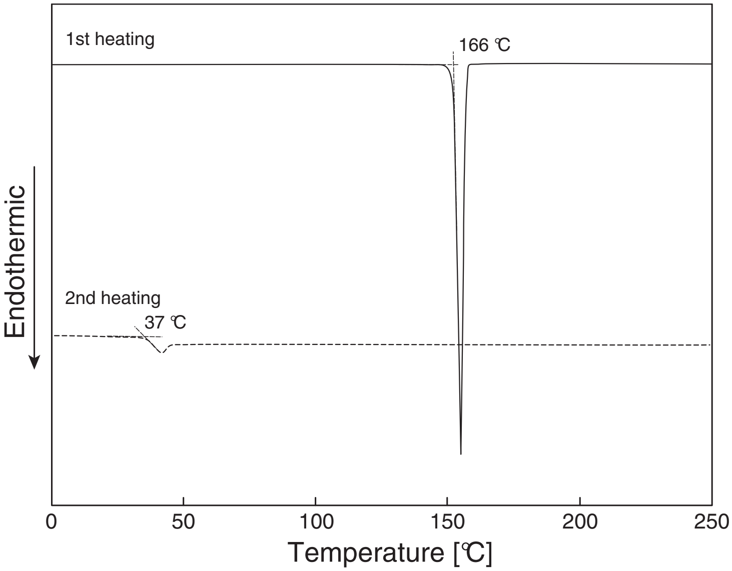


*Figure 3.*
DSC curves of **POSS-Cz**.

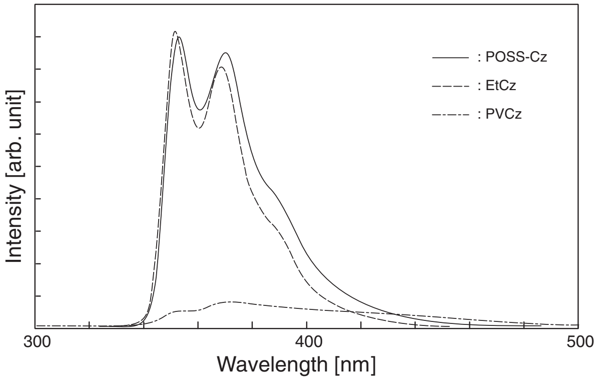


***Figure 4.***
Photoluminescence spectra of **POSS-Cz**, **EtCz**, and **PVCz** in dilute solution ($1 \times 10^{-6}$ mol dm$^{-3}$ in THF).

than those of **POSS-Cz** and **EtCz**. It is well-known that carbazole of **PVCz** can easily form excimer to result in low quantum yield. In the case of **POSS-Cz**, each carbazole seems to be isolated by the rigid core, so that the formation of excimer is prevented.

Photoluminescence spectra of **POSS-Cz** and **EtCz** in solid state were also investigated (Figure 5). Emission peak of **EtCz** shifted to long wavelength region due to the aggregation. On the other hand, **POSS-Cz** showed monomeric emission peak at the wavelength region from 350 to 400nm, although the structure of emission peak of solid **POSS-Cz** is slightly different from that in solution. The emission at around 450nm due to the aggregation is slightly clearer in crystalline **POSS-Cz** than that in amorphous **POSS-Cz**, but interestingly, monomeric emission peak was still strong in crystalline **POSS-Cz**. It suggests that carbazole moiety is isolated even in crystalline state, although the interaction between carbazole chromophores in crystalline state seems to be slightly stronger than in amorphous state. The absolute quantum yields of photoluminescence of both

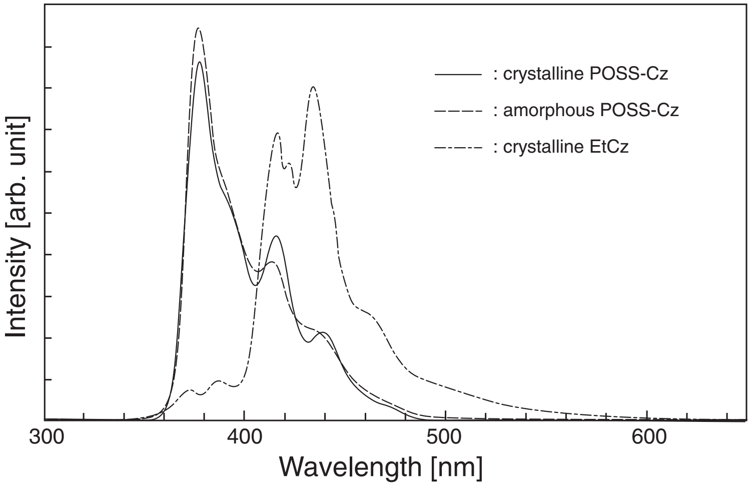


***Figure 5.***
Photoluminescence spectra of **POSS-Cz** and **EtCz** in solid state.

amorphous and crystalline states were estimated by a calibrated integrating sphere system, and they were found to be same ($\phi_{\text{crystallinePOSS}} = \phi_{\text{amorhousPOSS}} = 0.21$ at $\lambda_{\text{ex}} = 250$nm). The result suggests that the morphology of the POSS does not strongly affect to the aggregation of carbazole moiety. The introduction of more rigid spacer will suppress the aggregation of the material suitable to be fabricated in a solid-state device, which is now under investigation.

## Summary

Octasilsesquioxane having carbazole as a photo- and electroactive chromophore has been synthesized and investigated on its morphology and photoluminescence properties in solid state. It was found that the introduction of silsesquioxane core increases the thermal stability and induces to the amorphous glassy material. Also, the introduction of insulating and rigid silsesquioxane core isolates each carbazole moiety by both steric and electronic effects, to prevent the aggregation. These results will give a useful concept to develop novel class of photo- and electroactive materials.

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