Unique Photoluminescence Property of a Novel POSS-based Material Having Carbazole

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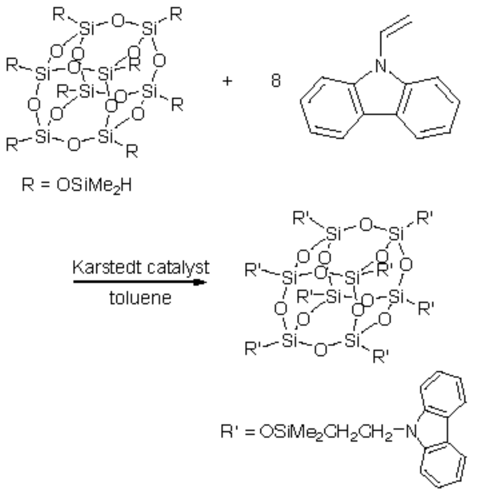
Introduction

Polyhedral oligomeric silsesquioxane (POSS) is a Si-O based materials with well-defined cage structures, and has been recently attracting a great deal of attention from the viewpoint of materials science. Eight silicon atoms of the POSS materials have three Si-O bonds and one Si-R bond, so that one organic functional group can be introduced on each silicon atom of POSS. Moreover, the introduced organic group can be isolated by steric and electronic effects, due to the rigid and bulky core and non-conjugated nature of siloxane bond. Thus, the introduction of photo- and electroactive π-electron system is expected to show unique optical and electrical properties, because the problems of aggregation in solid state film due to π-π interactions, such as crystallinity and formation of dimers, can be solved. However, there are few reports on the introduction of photo- and electroactive π-electron chromophores into the POSS system.

We report here on the first synthesis of perfectly substituted POSS with a carbazole group as one of photo- and electroactive π-chromophores, and on its thermal, morphological and optical properties.[1]

Carbazole unit was introduced into dimethylsiloxy group of octakis(dimethylsiloxy)silsesquioxane by hydrosilylation reaction with 9-vinylcarbazole (**VCz**) in the presence of platinum catalyst (Scheme 1). When H_2PtCl_6 was used as a catalyst, **VCz** was perfectly consumed, but the objective compound was not obtained, and instead, polymeric materials, which may be poly(9-vinylcarbazole) (**PVCz**), was obtained. This result suggests that H_2PtCl_6 will act as an initiator of polymerization of **VCz**. The use of platinum-divinyltetramethyldisiloxane complex, so called Karstedt catalyst, gave the desired compound, octakis[2-(carbazol-9-yl)ethyldimethylsiloxy]silsesquioxane (**POSS-Cz**) in the mild condition.



Scheme 1. Synthesis of **POSS-Cz**.

Very recently, He [2] and Sellinger [3] have independently reported the synthesis of POSS having photoemissive and hole-transport moieties. However, chemical structures of the POSS synthesized in their report is not well-controlled (number and position of substituents are not controlled.). ^{1}H, ^{13}C, ^{29}Si NMRs and MALDI-TOF MS spectra of **POSS-Cz** showed very clear signals and suggests that **POSS-Cz** is pure and its chemical structure is perfectly controlled.

Thermal properties of **POSS-Cz** were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC), and were compared with **PVCz** and 9-ethylcarbazole (**EtCz**). **POSS-Cz** was found to be stable until 400 °C, which is higher than **PVCz**. DSC of **POSS-Cz** in the first heating process showed only one sharp endothermic peak at 166 °C due to the melting behavior, but in the second heating process it showed only base-line shift at around 37 °C due to the glass-transition behavior.

Electronic absorption and photoluminescence spectra of dilute solutions (1×10^{-6} mol dm^{-3} in THF) of **POSS-Cz**, **EtCz** and **PVCz** were investigated. Electronic absorption spectrum of **POSS-Cz** showed two peaks at 332 and 347 nm due to the π-π* absorption (B-band) of carbazole, which is quite similar to that of **EtCz** (λ_{max} = 332 and 346 nm). Photoluminescence spectrum of **POSS-Cz** showed two peaks at 353 and 370 nm, which was the mirror image of the electronic absorption spectrum. This result is also similar to that of **EtCz**. Quantum yield of **POSS-Cz** in air was estimated by referring that of *p*-terphenyl ($\phi_{p\text{-terphenyl}}$ = 0.87), to be $\phi_{POSS\text{-}Cz}$ = 0.27, which is almost same as that of **EtCz** (ϕ_{EtCz} = 0.30). Although the electronic absorption spectrum of **PVCz** is similar to those of **POSS-Cz** and **EtCz** (λ_{max} = 331 and 344 nm), the photoluminescence spectrum of **PVCz** is quite different and broad, with quantum yield (ϕ_{PVCz} = 0.10) much lower 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.

Interestingly, the photoluminescence spectra of **POSS-Cz** in solid film showed mainly similar monomeric emission peak, while those of **EtCz** and **PVCz** showed broad peaks due to the formation of excimer by aggregation (Figure 1). This result suggests that the carbazole in **POSS-Cz** is almost isolated even in the solid state, different from **EtCz** and **PVCz**.

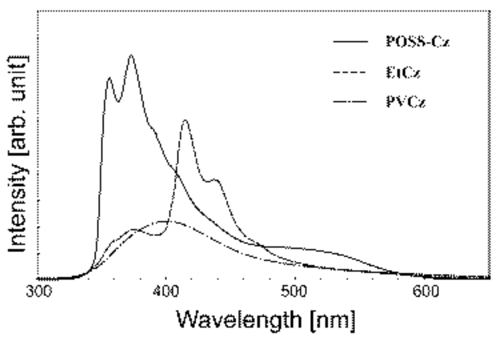


Figure 1. Photoluminescence spectra of **POSS-Cz** (solid), **EtCz** (dash), and **PVCz** (dash-dot) in solid film.

References

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[2] (a) He, C.; Huang, J.; Lin, T.; Mya, K. Y.; Zhang, X. *J. Am. Chem. Soc.* **2004**, *126*, 7792; (b) Xiao, Y.; Liu, T.; He, C.; Chin, W. S.; Lin, T.; Mya, K. Y.; Huang, J.; Lu, X. *J. Mater. Chem.* **2006**, *16*, 829.
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