

Electronic Supplementary Information

High Photo- and Electroluminescence Efficiencies of Ladder-like Structured Polysilsesquioxane with Carbazole Groups

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Materials. Carbazole (Cica; 95%) was purified by recrystallization from ethanol before use. 3-bromopropyltrimethoxysilane (BPTMS) (Gelest) was distilled before use. Dimethylformamide (DMF) (J.T Baker; 99.8%) was distilled from calcium hydride before use. Potassium carbonate (K₂CO₃) (sam-jun) was dried overnight over vacuum at 50 °C before use. Polyvinylcarbazole (PVK) (Aldrich, *M_n* 25,000~50,000) was used without purification.

Characterization of synthetic PPCSQ. The average molecular weight (*M_n*) and molecular weight distributions (*M_w*/*M_n*) of the polymers were measured using a JASCO PU-2080 plus SEC system equipped with RI-2031 plus refractive index detector and a UV-2075 plus UV detector (254 nm detection wavelength) using THF as the mobile phase at 40 °C and a flow rate of 1 mL/min. The samples were separated through four columns (Shodex-GPC KF-802, KF-803, KF-804, and KF-805). ¹H and ²⁹Si spectra were recorded in CDCl₃ at 25 °C on a Varian Unity INOVA (¹H: 300 MHz,

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^{29}Si : 99.5 MHz). The differential scanning calorimeter was measured using a TA instrument DSC 2910 under nitrogen. Thermal gravimetric analysis was performed using a TA Instrument TGA 2950 under nitrogen. Ultraviolet-visible (UV-vis) spectroscopy absorption and photoluminescence spectra were measured in air with a VALOR-III spectrophotometer (JASCO) and a V-570 spectrophotometer (JASCO), respectively. Thicknesses of the PPCSQ and PVK film were about 2000 Å, as measured with a KLA- Tencor Alpha-step IQ surface profiler. The X-ray film diffraction was examined at the beam-line 3C2 of Pohang light source (PLS) in the Pohang Accelerator Laboratory (PAL) using Cu-K α radiation. For surface imaging of the PPCSQ a Digital Instruments Nanoscope-IIIa multimode scanning probe microscope was used and operated in tapping mode.

Device Fabrication Method. EL devices were fabricated on indium tin oxide(ITO)-coated glass substrates that were cleaned and treated with oxygen plasma before use. A layer of PSS:PEDOT with a thickness of 20 nm was first spin coated on the treated substrate, and annealed at 120 °C for 1 h in a vacuum. Then, blends of PVK or PPCSQ with *fac-tris*[2-(2-pyridinyl-kN)[5-(2,5-dimethylphenyl)dphenyl]phenyl]-kC]-iridium(III) [Ir(PDPP) $_3$] in a chlorobenzene solution (10 mg/mL) were spin coated on top of the substrate precoated with PSS:PEDOT layer. For the ITO/PEDOT/PPCSQ or PVK:Ir(PDPP) $_3$ blend/BCP/Li:Al device, a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline(BCP) layer (10 nm) as a hole blocking layer was thermally evaporated onto the blend layer at below 1×10^{-6} Torr before electrode deposition, and then, a cathode layer of 150-nm-thick Li:Al alloy was vacuum deposited at 1×10^{-6} Torr.

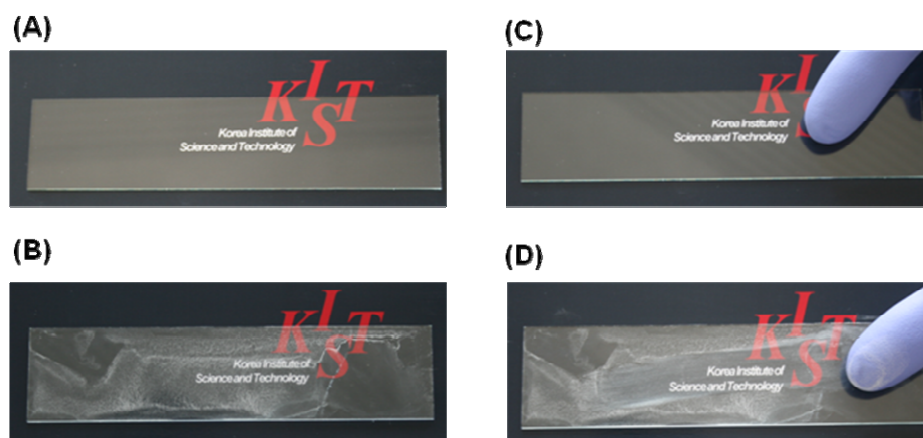


Figure S1. Thin film image on the glass of PPCSQ (A and C) and DPPOSS (B and D): A and B after spin coating; C and D after rubbing of the films by finger.

Film forming properties of PPCSQ and similarly functionalized POSS (Dodeca phenyl polyhedral oligomeric silsesquioxane, DPPOSS) phenyl-POSS) were examined. Figure S1, A-B shows spin coated PPCSQ and DPPOSS on a glass, respectively (0.5 wt.% in THF and spin rate = 2000 rpm). The film of the PPCSQ showed optically clear and transparent, while that of the DPPOSS showed hazy and mottled film, which was rather like powder on the glass. Figure S1, C-D shows the status after rubbing of the samples by finger in Figure S1, A-B, respectively. It clearly showed that the PPCSQ was able to withstand to such physical force, while DPPOSS was broke down under the same condition.

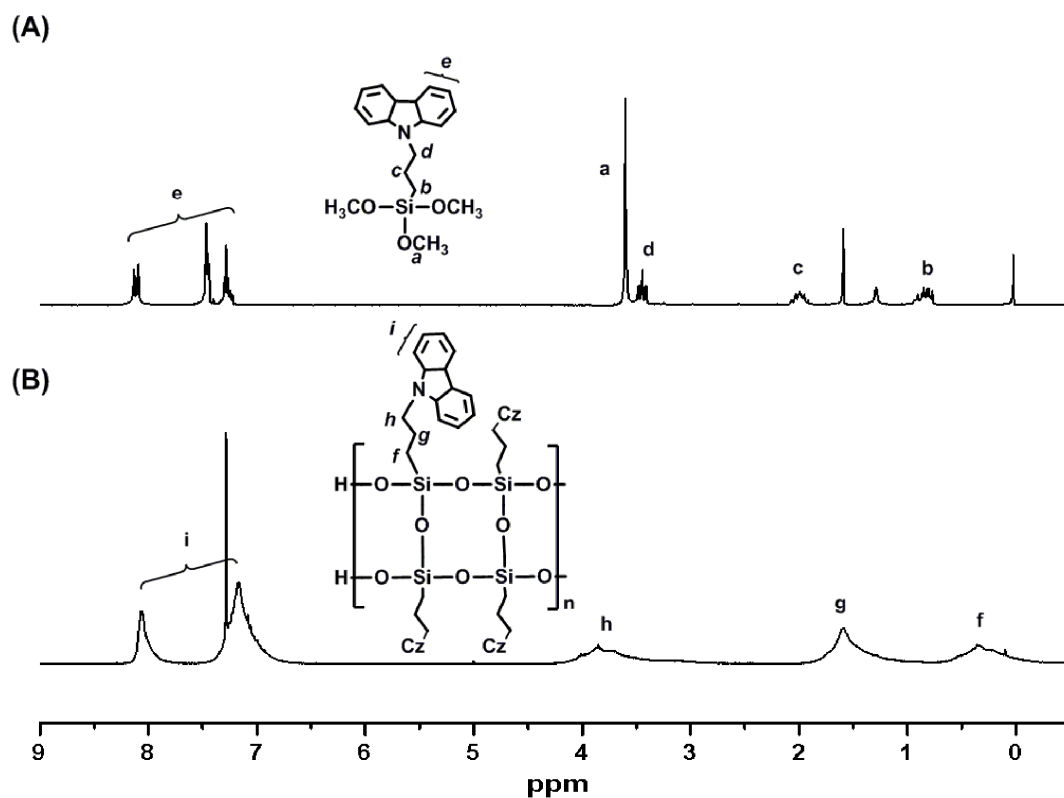


Figure S2. ^1H NMR spectra of 9-[3-(trimethoxysilyl)propyl]-9H-carbazole (1) (A) and PPCSQ (3) (B) in CDCl_3 .

Figure S2A and S2B showed ^1H NMR spectra of the precursor monomer and obtained PPCSQ, respectively. Disappearance of the proton peak (a) of the trimethoxy group of synthetic monomer in Figure S2A and broad shapes of the proton peaks (f–i) originated from the propyl carbazole groups of PPCSQ in Figure S2B.

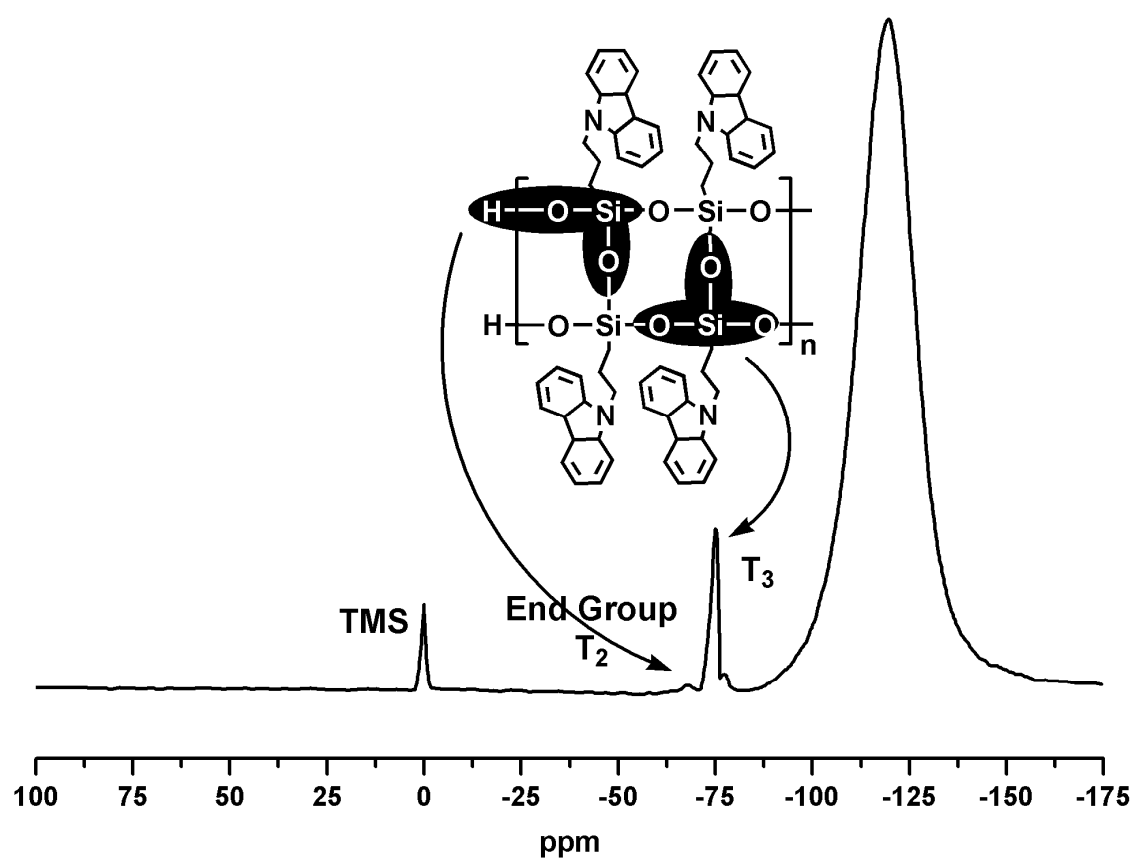


Figure S3. ^{29}Si NMR spectrum of PPCSQ (3) in CDCl_3 .

Figure S3 shows ^{29}Si NMR spectra of the obtained PPCSQ. Large absorption peaks ranged from -70.6 to -79.2 ppm and an adjacent small absorption peak in the downfield indicated the T_3 structure $[\text{R}-\text{Si}(\text{OSi})_3]$ and T_2 structure $[\text{R}-\text{Si}(\text{OSi})_2(\text{OR}')]_n$ of the siloxane backbone in PPCSQ, respectively.

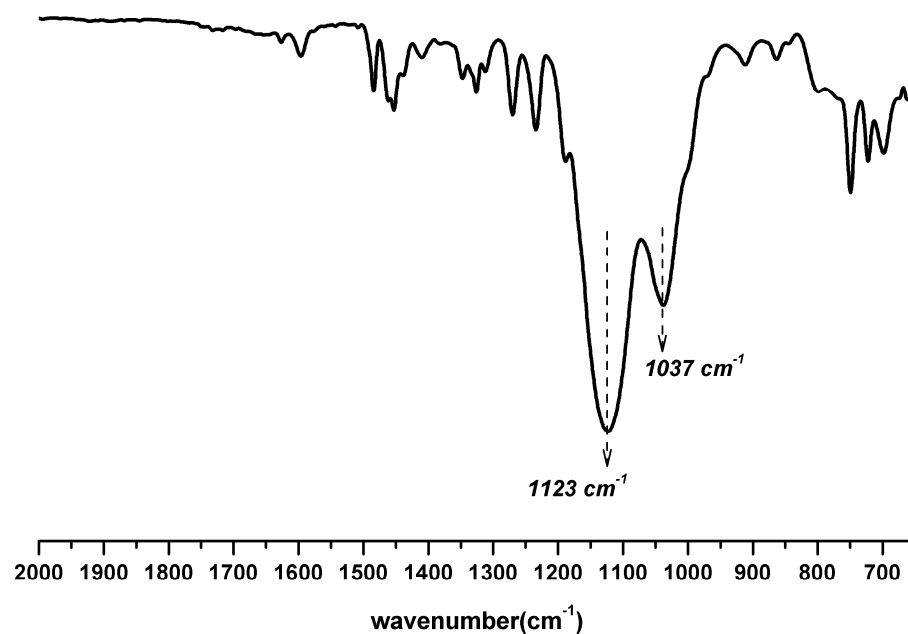


Figure S4. FT-IR spectrum of PPCSQ.

The FT-IR spectrum of PPCSQ is shown in Figure S4. Strong and broad absorption bands attributed to asymmetric Si-O-Si stretching were observed at 1123 cm⁻¹ and 1037cm⁻¹. In general FT-IR analyses of polysilsesquioxanes, closed cage structures such as polyhedral oligomeric silsesquioxanes (POSS) show one strong absorption peak near 1100 cm⁻¹ while two absorptions appear for ladder structures near 1150 cm⁻¹ and 1050 cm⁻¹ as bimodal shape. In figure S4, bimodal absorption peaks of PPCSQ showed a similar pattern with relation to the precedent ladder-type silsesquioxane studies.^{1,2}

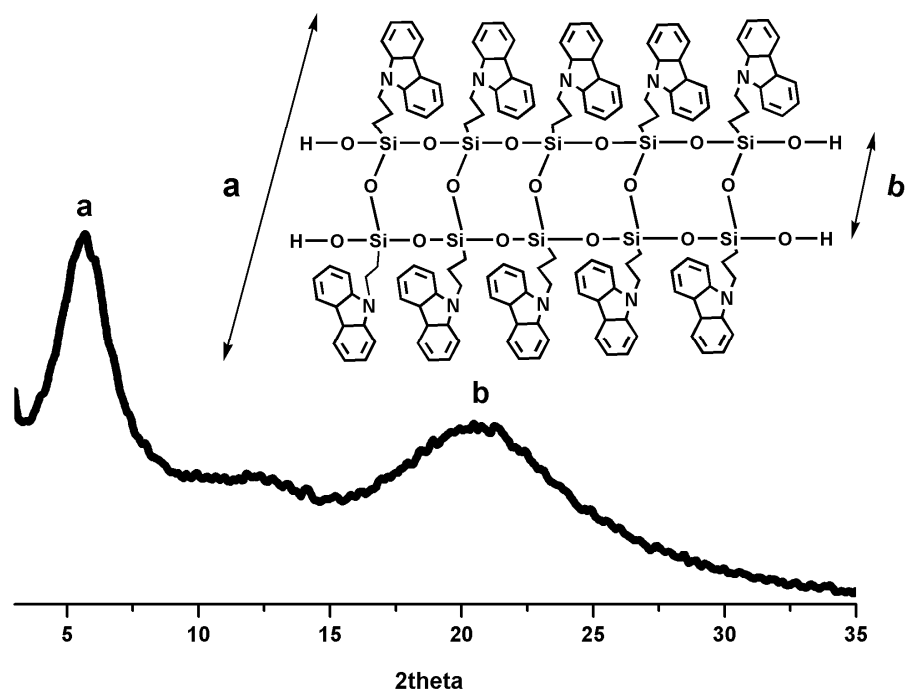


Figure S5. XRD pattern of PPCSQ: periodic chain-to-chain distance (a) and thickness (b).

X-ray diffraction (XRD) analysis carried out to investigate the detailed structure of the PPCSQ (Figure S5). Two characteristic diffraction peaks appeared at 5.66° (a) and 20.6° (b), respectively. The first sharp peak (a) was characteristic of the intramolecular periodic chain-to-chain distance ($d_1 = 15.6 \text{ \AA}$), thus the distance between two carbazole pendant groups through the ladder structured siloxane backbone, while the second diffused peak (b) indicated the average thickness of the siloxane backbone ($d_2 = 4.3 \text{ \AA}$).

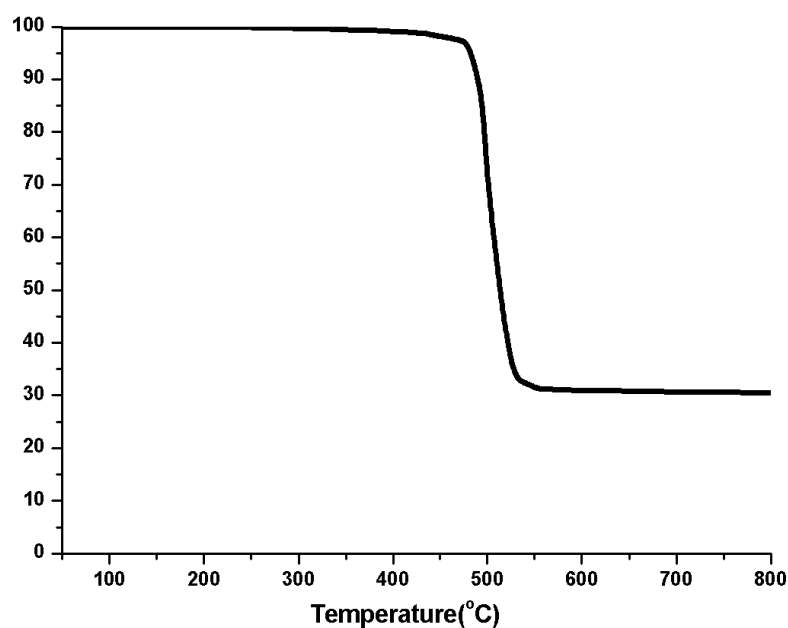


Figure S6. TGA thermogram curve of PPCSQ.

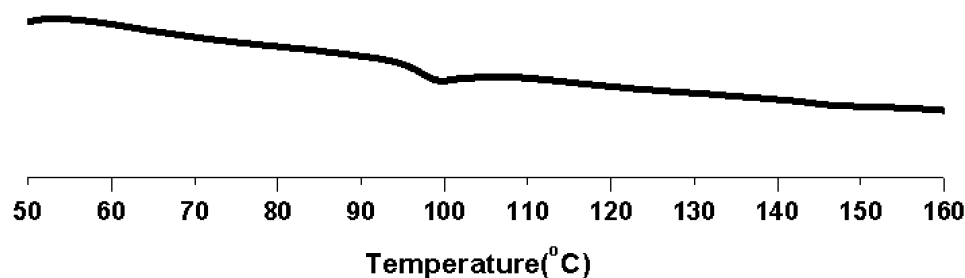


Figure S7. DSC curve of PPCSQ.

Figure S6 shows the TGA result with a 10 °C/min scan rate from 25 °C to 800 °C under nitrogen. Slight weight loss (~3%) occurred from 300 °C to 450 °C, probably due to decomposition of small amounts of the hydroxyl group at the end of the PPCSQ chain. Then, the weight was sharply decreased until 580 °C (~60%) by decomposition of the propyl carbazole groups. The remaining 35% of weight was stable until 800 °C, which was probably a residue of silica compound. DSC analysis was carried out between 50 °C and 160 °C with a 10 °C/min scan rate under nitrogen. Obtained DSC curve showed a single glass transition temperature (T_g) at 95 °C in the second heating (Figure S7).

References

1. H. Seki, T. Kajiwara, Y. Abe and T. Gunji, *Journal of Organometallic Chemistry*, 2010, **695**, 1363-1369.
2. M. Unno, A. Suto and H. Matsumoto, *Journal of the American Chemical Society*, 2002, **124**, 1574-1575.