Stabilized Blue Luminescent Polyfluorenes: Introducing Polyhedral Oligomeric Silsesquioxane

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ABSTRACT: A new POSS (polyhedral oligomeric silsesquioxane)-substituted polyfluorene was synthesized from the nickel-catalyzed Yamamoto coupling reaction. The synthesized polymers could be well characterized by ^{1}H NMR, FT-IR, and elemental analysis. PL spectra of PFPOSSs on the quartz film showed reduced aggregation/excimer formation because the bulky POSS group prohibited interchain interactions. This effective dilution effect and the high thermal stability of the POSS unit also improved the color stability of PFPOSSs blue emission even after thermal annealing at 150 °C. The fluorescence quantum yields (Φ_{FL}) of PFPOSSs in both solution and solid state were higher than those of poly(dialkylfluorene)s. Moreover, the ITO/PEDOT-PSS/polymer/Ca/Al LED device using this polymer as emitting layer showed a very stable blue light emission. LED devices of PFPOSSs showed a low turn-on voltage of 3.7−4.4 V, high brightness of 350−1010 cd/m^2, and external efficiencies of 0.11−0.36%.

Introduction

The development of electroluminescent polymers for the fabrication of full-color organic displays has given rise to intense academic and industrial research in this area.[1−3] One area of ongoing research is the quest for a stable blue-emitting material. Polyfluorene and its derivatives are the preferred conjugated polymers in blue light-emitting applications because of their thermal and chemical stability, good solubility in the common organic solvents, and high fluorescent quantum yields in the solid state.[4−6] However, the problems encountered with the use of poly(9,9-dialkylfluorene)s as blue emitters in light-emitting diodes (LEDs) are the undesirable lower-energy emission bands leading to blue-green emission and fluorescence quenching. To avoid this detrimental behavior, a number of approaches have been used. One approach is to introduce end-capped polyfluorenes with a bulky group,[7,8] a spirofluorene-functionalized bifluorene moiety,[9,10] networking polyfluorenes,[11] and dendron side groups into the C-9 position of polyfluorenes[12] as well as minimizing the isolated fluorenone defects.[21] Although there have been significant advances toward stable blue-emitting polyfluorene, more stabilized color purity needs improvement for commercialization of full-color displays.

Polyhedral oligomeric silsesquioxanes (POSS), with their unique cagelike structures and nanoscale dimensions, are of particular interest in the field of hybrid materials, and organic−inorganic hybrid polymer systems containing POSS moieties have been used because of the inorganic nature and multiple reactive functionalities of POSS. Incorporation of POSS as a pendant group of a linear polymer increases thermal and mechanical stability of the polymer, including increasing resistance to atomic oxygen in air, and also reduces flammability, density, and viscosity.[13]

We report here a novel method for preparing a new type of fluorene−POSS organic−inorganic hybrid polymer, in which POSS units are used as a pendant group. This is the first trial that a nanosized POSS unit has been incorporated as a pendant unit of a conjugated polymer. We have studied both the PL and EL from PFPOSSs and found that this polymer shows much stabilized blue emission and high performance.

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Experimental Section

Measurements. 2,7-Dibromofluorene, 1-bromohexane, 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, tetrabutylammonium bromide, tetrabutylammonium bromide (TBAB), toluene, *tert*-butyllithium, 2,2′-dipyridyl, 1,5-cyclooctadiene, and 1-(hydridodimethylsilyloxy)-3,5,7,9,11,13,15-heptacyclopentylpentacyclo-[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]octasiloxane were obtained from Aldrich Chemical Co. and used without further purification. Bis(1,5-cyclooctadienyl)nickel(0) was purchased from STREM Chemicals. Sodium hydroxide was purchased from Junsei Chemical Co., and all other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification.

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 and 400 spectrometer, respectively, with tetramethylsilane as an internal reference. For the NMR measurements, chloroform-*d* ($CDCl_3$) was used as the solvent. FT-IR spectra were obtained using a Nicolet model 800 spectrometer with samples prepared as KBr pellets. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150C instrument, using THF as eluent and polystyrene as standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the polymers were performed under a nitrogen atmosphere at a heating rate of 10 °C/min using a Dupont 9900 analyzer. UV−vis spectra were measured on a Jasco V-530 UV/vis spectrometer, and PL spectra of the polymers were measured at room temperature on a Spex Fluorolog-3 spectrofluorometer (model FL3−11) using spin-coated films. Elemental analyses were performed by the Korea Basic Science Institute. Cyclic voltammetry was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in a solution of Bu_4NBF_4 (0.10 M) in acetonitrile at a scan rate of 50 mV/s. A film of each polymer was coated onto a Pt wire electrode by dipping the electrode into a solution of the polymer (0.5 wt % in *p*-xylene). Film thickness was measured with a TENCOR alpha-step 500 surface profiler. Electroluminescence spectra were obtained with a Minolta CS-1000. Current−voltage and luminance−voltage were recorded on current−

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voltage source (Keithley 238) and a Minolta LS-100. Films of the polymers were prepared by spin-coating solutions of 10 mg mL^{-1} of polymer in anhydrous dichlorobenzene (Aldrich) at 1500 rpm.

Syntheses of Monomers. Preparation of 2-{2-[2,7-Dibromo-9-(2-perhydro-2*H*-pyran-2-yloxyethyl)fluoren-9-yl]ethoxy}perhydro-2*H*-pyran (1). To a solution of 29.18 g (90 mmol) of 2,7-dibromofluorene, 48.78 g (235 mmol) of 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, 50 mL of toluene, and 1.2 g of tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst was added 50 mL of a 50 wt % NaOH aqueous solution. The reaction mixture was then refluxed at 100 °C for 10 h. After cooling, extraction with 200 mL of ethyl acetate, 200 mL of saturated sodium bicarbonate, and water, dried over anhydrous magnesium sulfate, and then concentrated in vacuo. Pure viscous oil (**1**) 31.10 g (53.6 mmol, yield 59.5%) was obtained via chromatography on silica gel. Anal. Calcd for $C_{27}H_{32}Br_2O_4$: C, 55.88; H, 5.56. Found: C, 55.74; H, 5.57. ^{1}H NMR ($CDCl_3$, ppm): 1.20−1.66 (m, 12H), 2.34 (t, 4H), 2.68−3.14 (m, 4H), 3.22−3.48 (m, 4H), 4.08 (t, 2H), 7.39−7.52 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm): 19.16, 25.28, 30.36, 39.82, 52.44, 61.75, 63.28, 98.64, 121.08, 121.48, 126.96, 130.47, 138.67, 151.24.

Preparation of 2-[2,7-Dibromo-9-(2-hydroxyethyl)-hexylfluoren-9-yl]ethan-1-ol (2). To 17.41 g (30 mmol) of the THP-protected fluorene compound **1**, 100 mL of acidified ethanol (containing 5 mL of a 10% HCl aqueous solution) was added, and then the reaction mixture was refluxed for 30 min. After cooling, the ethanol was removed by rotary evaporation in vacuo at 60 °C. Extraction with chloroform and washed with a saturated aqueous sodium bicarbonate solution and two 100 mL portions of water, then dried over anhydrous magnesium sulfate, and then concentrated in vacuo. Column chromatography on silica gel gave purified product, 12.6 g (25.6 mmol, yield 85.1%). Calcd for $C_{17}H_{16}Br_2O_2$: C, 49.54; H, 3.91. Found: C, 49.61; H, 3.94. ^{1}H NMR ($CDCl_3$, ppm): 2.16 (s, 2H), 2.21 (t, 4H), 2.83 (t, 4H), 7.36−7.47 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm): 42.2, 52.0, 58.0, 121.3, 121.7, 126.5, 130.8, 138.3, 151.0.

Preparation of 1-{2-[2,7-Dibromo-9-(1-prop-2-ene)fluoren-9-yl]ethoxy}prop-2-ene (3). The deprotected compound **2** (2.07 g, 6.5 mmol), ally bromide (1,9 g, 15.7 mmol), and tetrabutylammonium bromide (1.2 g) were dissolved in 20 mL of toluene. To this solution, 80 mL of a 50 wt % NaOH aqueous solution was added, and the reaction mixture was refluxed for 24 h. After being cooled, the resulting solution was extracted with ethyl acetate and distilled water and then dried with magnesium sulfate. The crude product was purified by column chromatography on silica gel, yielding 2.29 g (92.7%). Anal. Calcd for $C_{23}H_{24}Br_2O_2$: C, 56.12; H, 4.91. Found: C, 56.16; H, 4.89. ^{1}H NMR ($CDCl_3$, ppm): 2.32 (t, 4H), 2.77 (t, 4H), 3.57 (d, 4H), 5.03 (m, 4H), 5.63 (m, 2H), 7.43−7.54 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm): 39.6, 52.2, 66.0, 71.6, 116.5, 121.2, 121.7, 126.8, 130.7, 134.6, 138.6, 151.2.

Preparation of 2,7-Dibromo-9,9′-di-POSS Fluorene (Monomer I). A total of 1.02 g (2.08 mmol) of the vinylfluorene compound **3** and 4.05 g (4.16 mmol) of hydrido POSS was dissolved in 30 mL of toluene, and 1 g of Pt(dvs) was dispersed in the solution. The resulting solution was refluxed 24 h and then filtered through a medium-size glass filter packed with Celite-545. After evaporation in vacuo, the concentrated crude product was purified by column chromatography, yielding 3.4 g (67.0%) of the powder product: Anal. Calcd for $C_{97}H_{164}Br_2O_{28}Si_{18}$: C, 47.68; H, 6.76. Found: C, 48.47; H, 6.85. ^{1}H NMR ($CDCl_3$, ppm): 0.08 (s, 6H), 0.41 (t, 4H), 1.35 (m, 4H), 1.47 (m, 112H), 2.30 (t, 4H), 2.75 (t, 4H), 2.98 (t, 4H), 7.25−7.54 (m, 12H). ^{13}C NMR ($CDCl_3$, ppm): 13.7, 22.2, 23.15, 26.99, 27.28, 39.72, 51.95, 66.21, 121.16, 121.64, 126.63, 130.60, 138.50, 151.05.

Preparation of 2,7-Dibromo-9,9′-dihexylfluorene (Monomer II). To a solution of 24.92 g (76.9 mmol) of 2,7-dibromofluorene, 26.05 g (157.8 mmol) of 1-bromohexane, 50 mL of toluene, and 1.4 g of tetrabutylammonium bromide as a phase-transfer catalyst was added 50 mL of 50 wt % NaOH aqueous solution. The reaction mixture was then refluxed at 100 °C for 10 h. After the reaction was completed, the reaction mixture was cooled into ambient temperature. The resulting solution was extracted with 200 mL of methylene chloride from 200 mL of saturated sodium bicarbonate, washed with water, dried over anhydrous magnesium sulfate, and then concentrated in vacuo. The crude product was purified by recrystallization with *n*-hexane several times to give 34.75 g (yield 91.8%) of solid-state product. Anal. Calcd for $C_{25}H_{32}Br_2$: C, 60.99; H, 6.55. Found: C, 61.05; H, 6.64. ^{1}H NMR ($CDCl_3$, ppm): 0.58 (br s, 4H), 0.74 (t, 6H), 1.02−1.12 (m, 12H), 1.90 (m, 4H), 7.42−7.51 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm): 14.00, 22.58, 23.66, 29.59, 31.46, 40.21, 55.70, 121.13, 121.49, 126.20, 130.17, 139.08, 152.58.

Synthesis of Polymers. Preparation of PFPOSSs. A mixture of 0.735 g of bis(1,5-cyclooctadienyl)nickel(0), 0.417 g of 2,2′-dipyridyl, 0.2 mL of 1,5-cyclooctadiene, and 5 mL of anhydrous DMF was maintained at 80 °C for 30 min under an argon atmosphere. To this solution, a total of 1.8 mmol of monomers, comprising a mixture of 2,7-dibromo-9,9′-dihexylfluorene and 2,7-dibromo-9,9′-di-POSS fluorene (monomer I) in a respective molar ratio of 99/1, 98/2, 95/5, 90/10, and 80/20 dissolved in 15 mL of toluene, was added dropwise. The resulting solution was stirred at 80 °C for 3 days. Then, 0.1 g of 9-bromoantracene (the end-capper) in 5 mL of anhydrous toluene was added to the polymer solution, and the resulting solution was stirred at 80 °C for a further 24 h. After the reaction finished, each polymer was precipitated in a mixture of HCl, acetone, and methanol (vol % of 1:1:2). The filtered crude polymer was extracted with chloroform and precipitated in methanol. Finally, the resulting polymers were purified by Soxhlet extraction and dried in vacuo. The resulting polymer yields ranged from 64.8 to 83.2% (PFPOSS01, 83.2%; PFPOSS02, 73.5%; PFPOSS05, 73.3%; PFPOSS10, 64.8%; PFPOSS20, 70.3%). ^{1}H NMR ($CDCl_3$, ppm): 0 (m), 0.58 (m), 0.78 (t), 1.12 (m), 2.09 (m), 7.66−7.83 (m). FT-IR (KBr, cm^{-1}): 2954, 2927, 2856, 1458, 1402, 1377, 1250, 1107, 1033, 999, 885, 813, 758.

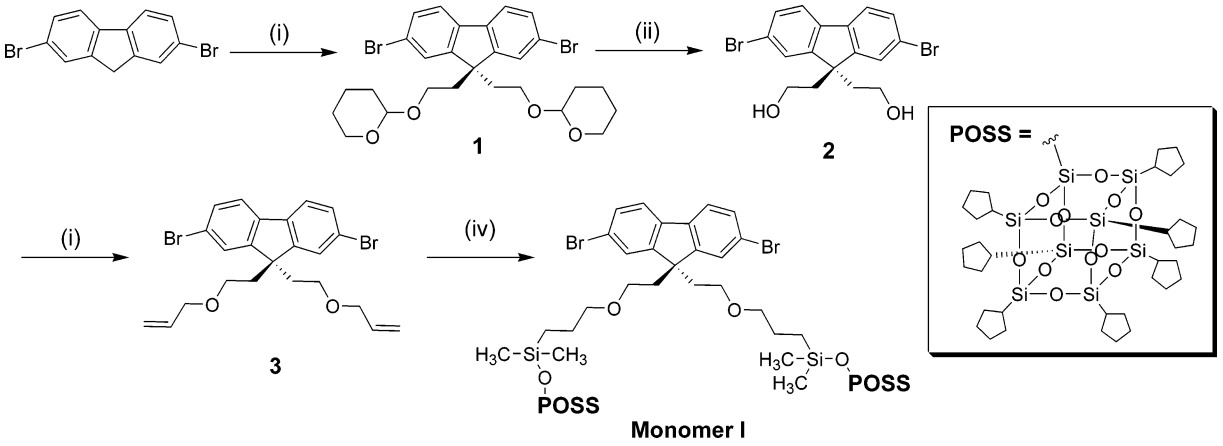
Preparation of Poly(9,9′-dihexylfluorene) (PDHF). The polymerization and purification procedure for PDHF was the same as those used for PFPOSSs; the polymerization yield is 67% for PDHF.[11b]

Results and Discussion

Synthesis and Characterization. Our approach is based on utilizing nanosized POSSs which can limit aggregation between polymer chain in the nickel(0)-mediated polymerization of 2,7-dibromo-9,9′-dialkylfluorene derivatives. The synthetic procedures for the monomer and the novel POSS-functionalized polyfluorene are shown in Schemes 1 and 2.

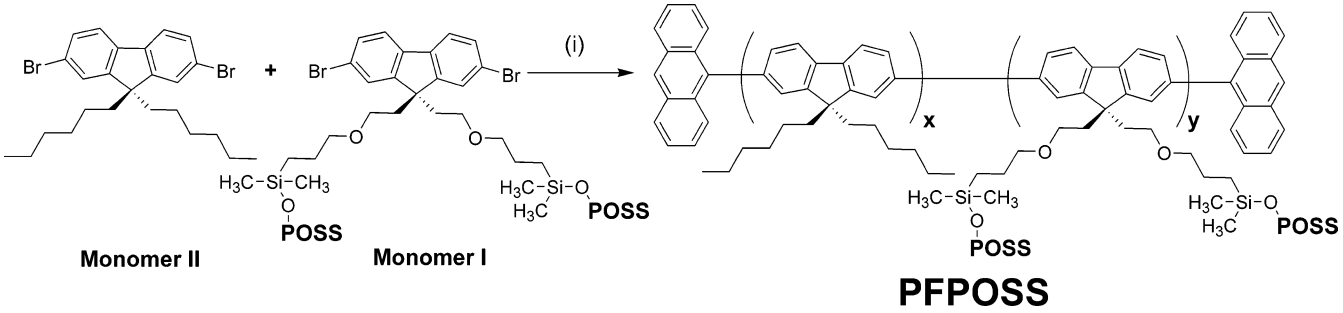
The synthesis of 2,7-dibromo-9,9′-diPOSS-substituted fluorene (monomer I) begins by alkylation of 2,7-dibromofluorene with 2-(2-bromoethoxyl)tetrahydro-2*H*-pyran, and then under acidic conditions **1** deprotected to give **2**. Both compounds **1** and **2** were purely separated by column chromatography. By allylation of **2** and then by hydrosilation reaction between **3** and monofunctional POSS, monomer I (bisPOSS-substituted monomer) was prepared. 2,7-Dibromo-9,9′-dihexylfluorene (monomer II) was synthesized by alkylation of 2,7-dibromofluorene. The nickel(0)-mediated Yamamoto polymerization has been used for the copolymerization of monomer I and monomer II (see Scheme 2). The molecular structures of monomers and polymers were confirmed by elemental analysis, ^{1}H NMR, and FT-IR spectroscopy. For PFPOSSs, their conventional proton peaks of Si−CH_3 groups in POSS units were observed near 0 ppm by ^{1}H NMR, and a strong Si−O stretching band at 1118 cm^{-1} was observed by FT-IR. Especially this strong Si−O stretching band near 1100 cm^{-1} is confirmation of cage structure Si−O−Si bonding; in other literature, the Si−O−Si stretching band of net-

Scheme 1. Synthetic Routes to the Monomers[a]



[a] (i) NaOH 50 wt % aq soln, toluene, TBAB, 2-(2-bromoethoxy)tetrahydro-2*H*-pyran2-(2-bromoethoxy)tetrahydro-2*H*-pyran, 100 °C, 8 h; (ii) HCl (several drops), ethanol, 80 °C, 20 min; (iii) NaOH 50 wt % aq soln, toluene, TBAB, allyl bromide; (iv) hydride-terminated POSS, toluene, Pt(dvs), 60 °C, 24 h.

Scheme 2. Synthetic Routes to the Polymers[a]



[a] (i) (a) $Ni(COD)_2$, COD, DMF, 2,2′-dipyridyl, toluene, 80 °C, 3 days; (b) 9-bromoanthracene, 80 °C, 24 h.

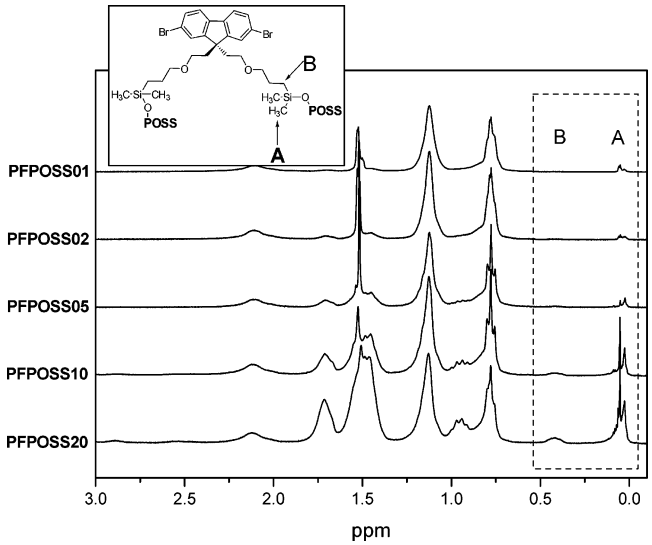


Figure 1. ^{1}H NMR spectra of PFPOSSs.

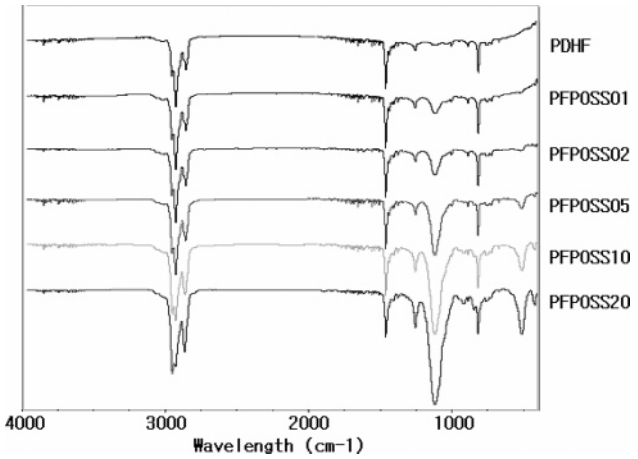


Figure 2. IR spectra of polymers.

work structure is near 1063 cm^{-1} and that of suboxide or strained ring is near 1023 cm^{-1}.[14] Upon increasing the POSS ratio, proton peaks near 0 ppm in the ^{1}H NMR spectra and Si−O stretching bands near 1100 cm^{-1} became more intensified (Figures 1 and 2).

POSS-substituted fluorene polymers showed very good solubility in common solvents such as chloroform, tetrahydrofuran (THF), toluene, *p*-xylene, and chlorobenzene without any gel formation. This good solubility of polymers is probably due to the introduction of a POSS unit that has seven cyclopentyl groups on the corner of POSSs. All the copolymers easily formed good films when solutions of the polymers in chloroform were cast on a glass substrate and the solvent was evaporated under air. The molecular weights were determined using gel permeation chromatography (GPC) against polystyrene standards with tetrahydrofuran (THF) as the eluent. The molecular weights and polydispersity index (PDI) values of the polymers are reported in Table 1. The molecular weights of PFPOSSs ranged from 17 600 to 30 600, and PDI values were from 2.00 to 2.22.

Thermal Properties. The thermal properties of PFPOSSs investigated using thermogravimetric analysis (TGA, heating rate of 10 °C/min) and differential scanning calorimetry (DSC, heating rate of 10 °C/min) are summarized in Table 1. The glass transition temperature (T_g) values for PFPOSSs (100, 101, 105, 103,

Table 1. Physical Properties of the Polymers

polymer	feed ratio (*x*/*y*)	yield (%)	M_n[a](10^4)	M_w[a](10^4)	PDI	T_g (°C)	T_d (°C)[b]
PDHF	100/0	67.0	3.12	10.53	3.38	75	421
PFPOSS01	99/1	83.2	3.06	6.49	2.21	100	422
PFPOSS02	98/2	73.5	2.20	4.66	2.12	101	422
PFPOSS05	95/5	73.3	2.02	4.32	2.14	105	417
PFPOSS10	90/10	64.8	1.81	4.01	2.22	103	414
PFPOSS20	80/20	70.3	1.76	3.52	2.00	108	406

[a] Determined by GPC, relative to polystyrene standards. [b] Temperature resulting in 5% weight loss based on initial weight.

Table 2. Optical Properties of the Polymers

	γ_{max} (UV, nm)		λ_{max} (PL, nm)		
polymer	solution	film	solution (Φ_{PL}[b])	film (Φ_{PL}[c])	E_g (eV, UV/nm)[a]
PDHF	386	383	414 (0.82)	423 (1.00)	2.91
PFPOSS01	386	385	414 (0.89)	423 (1.11)	2.91
PFPOSS02	385	385	414 (0.90)	423 (1.16)	2.91
PFPOSS05	385	386	414 (0.95)	422 (1.41)	2.91
PFPOSS10	385	387	413 (0.96)	421 (1.70)	2.91
PFPOSS20	384	389	413 (0.99)	421 (2.23)	2.91

[a] E_g, calculated from the onset values of the absorption spectra of the spin-coated film on quartz. [b] The solution fluorescence quantum yield were measured in chloroform relative to quinine sulfate (approximately 1×10^{-5} M) in 0.10 M H_2SO_4 as standard. [c] The film fluorescence quantum yields measured on quartz plates relative to PDHF assuming 1.00 for comparison (1 wt % in *p*-xylene).

and 108 °C) are higher than that of PDHF (75 °C)[11b] and increased with increasing POSS contents. The higher T_g values for PFPOSSs are attributed to that the nanosized POSS moiety of PFPOSSs hinders the motion of polyfluorene main chain.

The PFPOSSs exhibited good thermal stability. The decomposition temperatures for 5% weight loss (T_d) of the PFPOSSs were above 400 °C. It is evident that the incorporation of POSS moiety at the C-9 position of fluorene is also maintaining the high thermal stability of polyfluorene (TGA data are shown in the Supporting Information). T_d of the polymers is a little bit decreased as the POSS unit is increased because of the loose molecular packing due to the high content of bulky POSS.

Optical and Photoluminescence Properties. The UV−vis absorption and PL spectra of POSS substituted polyfluorenes as in solution and thin films on quartz plates are shown in Table 2. Thin films of the PFPOSSs were prepared by spin-coating on quartz substrates from *p*-xylene solution (c = 10 mg/mL) for 60 s at 2000 rpm. The maximum absorption wavelengths and spectral patterns as well as the PL spectra of PFPOSSs are not significantly different from those of PDHF. This result is consistent with the report that substitution of the C-9 position of fluorene units of a polyfluorene does not remarkably change the electronic structure of the polyfluorene.[16,17] PL spectra of PDHF in solid states exhibited additional green emission features compared to the PL spectra of PDHF in solution. This is because of the interchain aggregation tendency of poly(dialkylfluorene)s in solid states or some keto defects. However, PL spectra of thin films of PFPOSSs on quartz plates showed reduced additional green emission formation because the bulky POSS group prohibited interchain interaction and formation of fluorenone defect. This effective isolation effect and the high thermal and oxygen stability of the POSS unit also improved the color stability of PFPOSSs blue emission. To investigate the optical properties after thermal treatment, the films

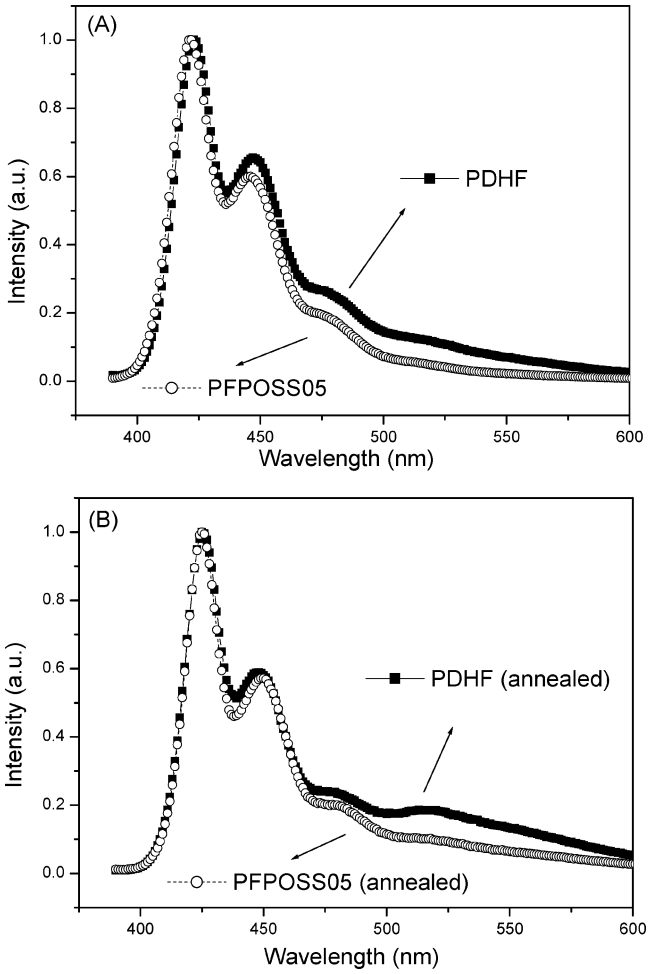


Figure 3. Comparison of PDHF and PFPOSS05 PL spectra before (A) and after (B) annealing at 150 °C for 5 h in air as spin-coated films.

on quartz plates were heated at 150 °C for 5 h in air and then cooled to room temperature[11b] (Figure 3). In the case of PDHF, an undesired green emission appeared around 500 nm. However, nanosized POSS-substituted polyfluorene (PFPOSS05) exhibited only pristine or highly reduced additional peaks even after thermal annealing. This is a result from the reduced formation of excimers/aggregation or lower concentration of fluorenone defects due to the bulky and highly resistant POSS units.[19,21]

The solution fluorescence quantum yield (Φ_{FL}) of PFPOSSs was almost up to 1.00 as measuring in chloroform relative to quinine sulfate (approximately 1×10^{-5} M) in 0.10 M H_2SO_4 as standard. The quantum yield after refractive index correction can be calculated according to refs 15 and 18. The relative Φ_{FL} value of PFPOSSs in the solid state is estimated by comparison with the fluorescence intensity of the PDHF thin film sample. In the solid state, Φ_{FL} of PFPOSS20 is twice

Table 3. Electrochemical Properties and Energy Levels of the Polymers

	p-doping (V)[a]						
polymer	E_{onset}	E_{pa}	E_{pc}	$E_{1/2}$	E_g (eV, UV/nm)	HOMO (eV)[b]	LUMO (eV)[c]
PDHF	0.98	1.03	0.97	1.00	2.91	−5.81	−2.90
PFPOSS01	0.99	1.04	0.97	1.01	2.91	−5.82	−2.91
PFPOSS02	1.00	1.06	0.97	1.02	2.91	−5.83	−2.92
PFPOSS05	0.99	1.05	0.97	1.01	2.91	−5.82	−2.91
PFPOSS10	1.00	1.06	0.98	1.02	2.91	−5.83	−2.92
PFPOSS20	1.01	1.08	0.98	1.03	2.91	−5.84	−2.93

[a] E_{onset}, E_{pa}, E_{pc}, and $E_{1/2}$ stand for onset potential, anodic peak potential, cathodic peak potential, and the average of the anodic and cathodic peak potentials, respectively (scan rate: 50 mV/s). [b] Determined from E_{onset} (energy level of ferrocene to be −4.8 eV under vacuum). [c] Calculated from the HOMO and E_g.

Table 4. EL Spectra Data and Performance Characteristics of Devices

polymer	CIE coordinates (x,y)[a]	max luminance (cd/m^2)	max current efficiency (cd/A)	quantum efficiency (%)	threshold voltage (V)[b]
PDHF	(0.25, 0.29)	360	0.12	0.06	4.8
PFPOSS01	(0.21, 0.19)	350	0.15	0.11	4.4
PFPOSS02	(0.21, 0.18)	650	0.46	0.32	3.9
PFPOSS05	(0.21, 0.17)	1010	0.46	0.36	3.7
PFPOSS10	(0.19, 0.15)	600	0.29	0.21	3.8
PFPOSS20	(0.19, 0.14)	660	0.41	0.29	3.8

[a] Determined from the EL spectra (Figure 4). [b] Threshold voltage, defined as the voltage required to give a luminance of 1 cd/m^2.

higher than that of PDHF (Table 2). The efficient isolation effect of the nanosized volume of POSS moiety inhibits the interchain aggregation/quenching, and hence PFPOSSs exhibit an enhanced Φ_{FL} value as the ratio of POSS increases.

Electrochemical Properties. Electrochemical properties of the polymers including the HOMO and LUMO energy levels were investigated to characterize and compare the electronic properties of the polymers through cyclic voltammetry (CV). The cyclic voltammograms of the polymers measured through using a polymer-coated platinum electrode as the working electrode, a platinum wire as the counter electrode, and an $Ag/AgNO_3$ (0.10 M) as the reference electrode. CV was performed with these three electrodes immersed in a solution of 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous acetonitrile at room temperature under nitrogen with a scan rate of 50 mV/s. The measurements were calibrated using ferrocene (4.8 eV below the vacuum level)[22] as the standard and are listed in Table 3. From the first oxidation process, the HOMO energy levels of PFPOSS01, PFPOSS02, PFPOSS05, PFPOSS10, and PFPOSS20 were estimated to be −5.82, −5.83, −5.82, −5.83, and −5.84 eV, respectively; these values almost coincide with the HOMO energy level (−5.81 eV) of PDHF. Unfortunately, a reduction wave was hardly obtained. So the LUMO energy levels of the polymers were estimated from the onset of the absorption spectra of the copolymer films, and this is the common method of obtaining the LUMO energy level of polyfluorene derivatives. The LUMO energy levels of PFPOSS01, PFPOSS02, PFPOSS05, PFPOSS10, PFPOSS20, and PDHF were estimated as −2.91, −2.92, −2.91, −2.92, −2.93, and −2.90 eV, respectively. The band gap energy of the PFPOSSs and PDHF was obtained from the onset of the UV spectrum of each polymer; all the polymers exhibited band gap energy of 2.91 eV.[9] Thus, within the experimental measurement errors, PFPOSSs and PDHF have the almost same HOMO and LUMO energy levels and band gap energies. This result indicates that the POSS moieties of the PFPOSSs are not involved in the oxidation of the polymers and that the POSS units do not affect the redox properties of the fluorene copolymers compared to PDHF.

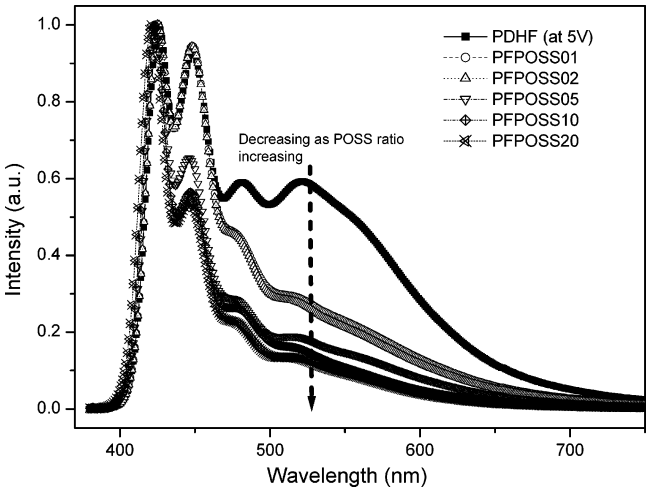


Figure 4. EL emission from device ITO/PEDOT:PSS/polymer-(80 nm)/Ca/Al at 5 V.

Electroluminescence Properties and Current−Voltage−Luminance Characteristics. The electroluminescence (EL) properties and the current−voltage−luminance characteristics (I−V−L) of the synthesized PDHF and PFPOSSs were measured at room temperature. A single-layer LED device with the configuration of ITO/PEDOT:PSS(40 nm)/polymer(80 nm)/Ca(500 nm)/Al(800 nm) was fabricated. The electroluminescence (EL) spectra showed that the emission falls in the blue region with the CIE coordinates from (0.21, 0.19: PFPOSS01) to (0.19, 0.14: PFPOSS20) (Figure 4 and Table 4). The EL device of PDHF showed a very intense additional band between 500 and 600 nm. However, the device constructed with PFPOSSs did not exhibit any significant long-wavelength emission in the EL spectrum, and undesired green emission over 500 nm was decreasing with increasing POSS ratio. Especially, the EL spectra of PFPOSS05, PFPOSS10, and PFPOSS20 showed very stable and durable blue emission with time or driven voltage, contrary to PDHF homopolymers.[20,21] The voltage−luminance (V−L) and voltage−current density (V−I) characteristics of the devices are shown

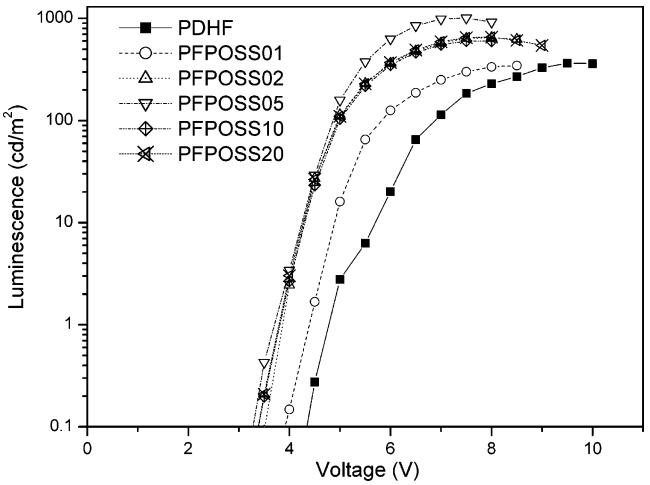


Figure 5. Voltage−luminance ($V-L$) characteristics of polymers.

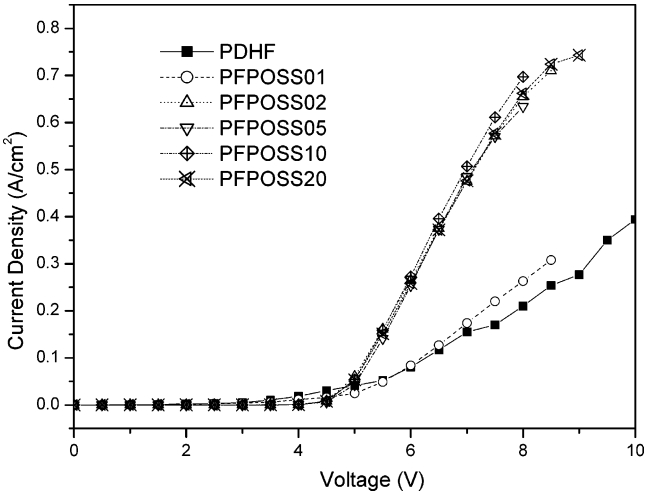


Figure 6. Voltage−current density ($V-I$) characteristics of polymers.

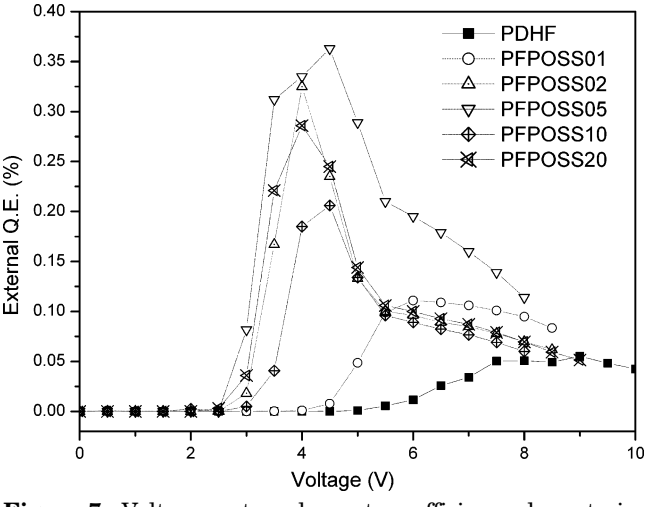


Figure 7. Voltage−external quantum efficiency characteristics of the devices.

in Figures 5 and 6, and their related performances are summarized in Table 4. The devices fabricated with PFPOSS showed slightly lower or similar turn-on voltages (V_T) in the range of 3.7−4.4 V compared to PDHF (4.8 V). Moreover PFPOSSs, as shown in Figure 7, exhibit apparently higher EL efficiencies. Especially a maximum external quantum efficiency of PFPOSS05 is 0.36%, which is 6 times higher than that of the PDHF (0.06%). The maximum luminance of PFPOSS05 for bright blue emission as depicted in Figure 5 is found to be 1010 cd/m^2 (as a bias of 7.5 V and a current density of 570 mA/cm^2); this is also a much higher value than that of PDHF (360 cd/m^2 as a bias of 9.5 V and a current density of 350 mA/cm^2). This is a much higher value than that of other alkyl-substituted polyfluorenes (polydioctylfluorene (PFO): maximum luminescence = 205 cd/m^2; polydiethylhexylfluorene (PF2/6): maximum luminescence = 99 cd/m^2).[23] The EL efficiency trend to the ratio of POSS is slightly different from that of PL efficiency. The EL efficiency of an LED depends not only on the PL efficiency of the active polymer but also on its charge injection balance and its carrier mobility.[23] The studies of this phenomenon and higher efficiency and brightness with better charge injection and more efficient charge recombination are underway.

Conclusion

In conclusion, highly efficient blue polymers, PFPOSSs, with nanosized POSS (polyhedral oligomeric silsesquioxane)-substituted polyfluorenes were synthesized. The incorporation of the POSS group inhibited interchain interaction and fluorenone formation, which leads to reduce undesired green emission (>500 nm) of poly(dialkylfluorene)s and to improve the thermal stability of PFPOSSs. Because of the POSS unit reduced the fluorescence quenching, the fluorescence quantum yields (Φ_{FL}) of PFPOSSs were also enhanced as the POSS ratio increased. The ITO/PEDOT-PSS/polymer/Ca/Al LED device using PFPOSSs as emitting layer showed a very stable blue light emission with high performance.

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Supporting Information Available: TGA thermograms of PFPOSSs; UV−vis absorption and PL spectra of polymers in solution and solid states. This material is available free of charge via the Internet at http://pubs.acs.org.

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