Highly Bright and Efficient Electroluminescence of New PPV Derivatives Containing Polyhedral Oligomeric Silsesquioxanes (POSSs) and Their Blends

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ABSTRACT: A new series of highly bright and efficient poly(*p*-phenylenevinylene)s (PPV)s based on polyhedral oligomeric silsesquioxanes (POSSs) was synthesized via the Gilch polymerization method. The three POSS-containing PPVs are as follows: POSS05-PPV(containing 5 mol % POSS-appended PPV units), POSS25-PPV, and POSS100-PPV (this is the first π-conjugated polymer composed of 100 mol % POSSs-appended repeating units). These polymers were found to be completely soluble in common organic solvents, and homogeneous thin films of these polymers were fabricated easily by spin-coating onto the quartz glasses and indium tin oxide (ITO) substrates. The POSS-containing PPVs exhibit higher glass transition temperatures (64−77 °C) than that of MEH-PPV (58 °C), indicating that electroluminescence (EL) devices fabricated with these polymers should have good thermal stabilities. The presence of the POSSs in the PPV side chains was found to result in the lowering of the maximum wavelengths of the UV−vis absorption and photoluminescence (PL) spectra, which occurs because of the nanosize effect of the POSS moieties appended to the polymer backbones. As the POSS content ratio in the polymers increases, the maximum wavelengths of the UV−vis absorption and PL emission spectra are increasingly blue-shifted except for those of POSS05-PPV. Light-emitting diodes (LEDs) with the configuration of ITO/PEDOT:PSS/polymer/Ca/Al were fabricated using the novel POSS-containing PPVs. The LED devices based on the POSS-containing PPVs were found to exhibit maximum EL wavelengths ranging from 577 to 543 nm (POSS05-PPV, 577 nm; POSS25-PPV, 575 nm; and POSS100-PPV, 543 nm). The LED devices containing POSS05-PPV or POSS25-PPV emitted orange-red light, whereas that containing POSS100-PPV emitted yellow-orange light. Interestingly, the maximum brightness and luminance efficiency of the POSS25-PPV device were found to be up to 6340 cd/m^2 at 13.2 V and 0.26 cd/A at 6190 cd/m^2, respectively, which are higher maximum brightness and luminance efficiencies than those of the MEH-PPV device (3880 cd/m^2 at 14.8 V and 0.075 cd/A at 3880 cd/m^2). The improvements in the EL properties of PPV derivatives that result from the introduction of the POSS moieties into the PPVs and the contribution of the POSS moieties to the conjugated polymer matrixes of EL devices were also reproduced in binary blend systems composed of a POSS-containing PPV (POSS25-PPV) and MEH-PPV. Surprisingly, the luminescence efficiency (0.48 cd/A at 10540 cd/m^2) of the binary blend consisting of 5 wt % of POSS25-PPV and 95 wt % of MEH-PPV was found to be enhanced by a factor of 6.4 with a maximum brightness of 11 010 cd/m^2 (at 14.3 V). It is likely that the enhanced device performance of POSS25-PPV and the binary blend consisting of 5 wt % of POSS25-PPV and 95 wt % of MEH-PPV are due to the formation of suitable insulation domains of the POSS moieties in the conjugated polymer matrixes, resulting in a balance of charge carriers, that is, of electrons and holes.

Introduction

Since the discovery by the Cambridge group of the potential applications of poly(*p*-phenylenevinylene) (PPV) as active light-emitting materials in flat-panel displays,[1] polymeric light-emitting diodes (PLEDs) have attracted much interest from academia and industry.[2] π-Conjugated polymers such as poly(*p*-phenylenevinylene) (PPV),[3−6] poly(*p*-phenylene) (PPP),[7] polythiophene (PT),[8] poly(thienylenevinylene) (PTV),[9] poly(*p*-phenyleneethenylene) (PPE),[10] polyfluorene (PF),[11−15] and their derivatives[16−18] have properties such as low operating voltages, good processability, and easy color tunability that are better for LED applications than those of low-molecular-weight organic materials. Among the many π-conjugated polymers that have been used in PLED applications, poly(*p*-phenylenevinylene)s (PPVs) and their derivatives have been the core materials.[3−6] However, it is well known that PPVs are poor electron acceptors because of their high LUMO energy levels, resulting in difficult electron injection and thus an imbalance in electron and hole injection.[19−24] The various proposed methods for overcoming the low electroluminescence efficiencies of these materials include: (1) the use of a metal with a low work function (e.g., calcium);[19] (2) the introduction of an electron-transporting layer between the light-emitting layer and the cathode;[20] (3) aligning the energy band gap of the polymer to emit light by introducing electron-withdrawing groups into the arylene ring or the vinylene moiety of PPV, thereby enabling the use of higher work function metals;[4e,21−22] (4) the introduction of 1,3,4-oxadiazole moieties as pendant groups or as part of the PPV main chains.[4b,23−24] In recent reports, the incorporation of polyhedral oligomeric

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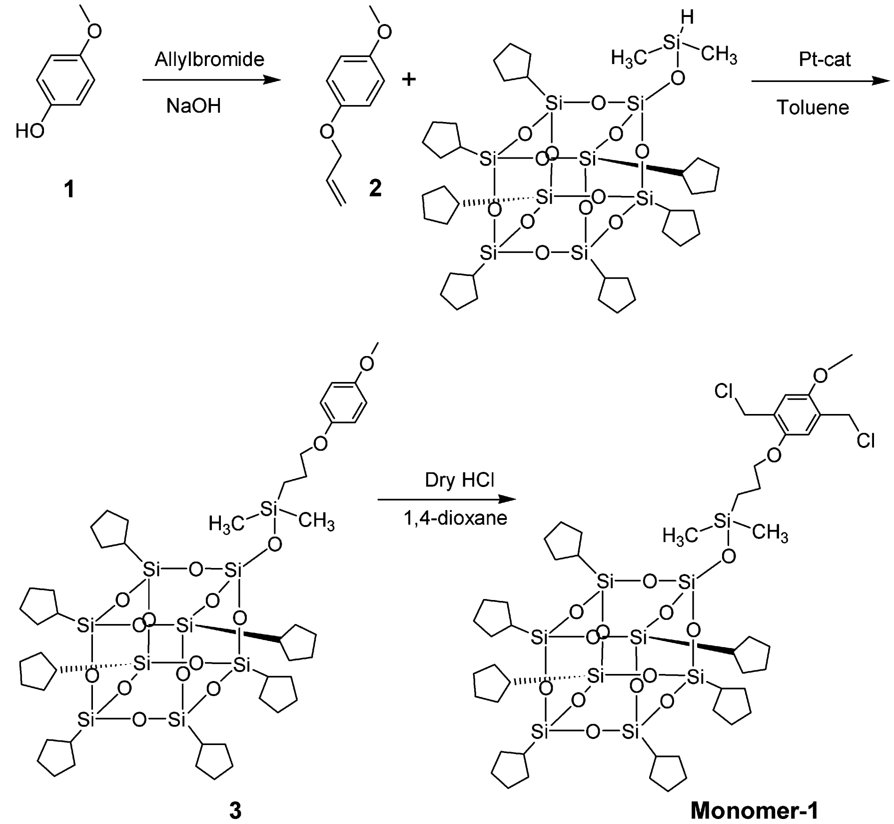
Scheme 1. Synthetic Route for the Monomer



silsesquioxane (POSS) moieties as end groups or side groups of π-conjugated polymers such as polyfluorenes has been proven to be effective in the enhancement of their photoluminescence (PL) and electroluminescence (EL) efficiencies because of the resulting suppression of excimer formation and aggregation and/or thermal oxidation, and the enhancement of intermolecular cross-linking between the polymer main chains.[25−30] Furthermore, the use of POSS units as nanocomposites or nanoparticles in EL devices has been explored.[36] Recently, Wei et al. demonstrated that the PL and EL properties of POSS-appended PPVs, in which a phenylene group lies between the arylene ring of PPV and the POSS moiety, are superior to those of MEH-PPVs.[31,32] We independently reported that POSS-containing PPVs exhibit better brightness and quantum efficiency than MEH-PPV in PL and EL studies.[31] In this paper, we report the incorporation of POSS groups as pendant groups of PPV derivatives, in which the flexible siloxane−trimethylene linkage lies between the arylene ring of PPV and the POSS moiety.[33] We also show that introducing POSS groups into the pendant groups of PPVs is a highly effective method for enhancing the PL and EL efficiencies of PPVs. In addition, we suggest that the use of a blend system composed of POSSs-containing PPV and MEH-PPV is the a facile and efficient method for improving the brightness (over 11000 cd/m^2) and quantum efficiency of EL devices fabricated with PPV derivatives.[34]

Synthesis and Characterization

In this study, the introduction of POSS units into the side groups of PPVs was the principal approach used to enhance the PL and EL efficiencies of PPVs.[29] The synthetic routes used to prepare the POSS-containing bis(chloromethyl)benzene monomers and the resulting POSS-containing PPV derivatives are presented in Schemes 1 and 2, respectively. We first synthesized compound **2** under basic conditions with an allylation reaction[4e] and then prepared compound **3** by hydrosilation of compound **2**.[15,29] Monomer **1**, the POSS-containing monomer, was finally synthesized by hydrochlorination of compound **3**; monomer **2** was prepared with the same reaction conditions as those used for monomer **1**.[4] The new POSS-containing bis(chloromethyl)-benzene monomer (monomer **1**) was synthesized successfully, as confirmed with elemental analysis, the ^{1}H NMR spectrum, and the ^{13}C NMR spectrum.[29] To obtain the POSS-containing copolymers, the final monomers (monomers **1** and **2**) were copolymerized via Gilch polymerizations with potassium *tert*-butoxide in THF solution.[4] Monomer **1** was homopolymerized for POSS100-PPV in the same condition, and monomer **2** for MEH-PPV. The resulting polymers were found to be tough fibers and completely soluble in common organic solvents such as dichloromethane, chloroform, THF, toluene, *p*-xylene, chlorobenzene, and the like. Furthermore, all of them could be spun-cast onto various substrates giving highly homogeneous and transparent thin films.[15] The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the copolymers (POSS05-PPV and POSS25-PPV) were 54 000−55 000 and 108 000−215 000, respectively, with a polydispersity of 2.0−3.9, as determined with GPC using THF as an eluent and polystyrene as a standard. The physical properties of the polymers are listed in Table 1. The chemical structures of the POSS-containing polymers were confirmed successfully with elemental analysis, and from the ^{1}H NMR and ^{13}C NMR spectra.[29] The ^{1}H NMR spectra of all of the synthesized polymers are shown in Figure 1. For the POSS-containing polymers, the proton peaks characteristic of the Si−CH and Si−CH$_2$ groups in the POSS units appear in the ^{1}H NMR spectra near 0.1 ppm.[29] The proton peaks near 0.1 ppm in the ^{1}H NMR spectra were found to increase in intensity with increases in the molar ratio of the POSS units in the polymers.[29] The POSS-containing monomer content ratio in the polymers was calculated

Scheme 2. Synthetic Routes for the Polymers

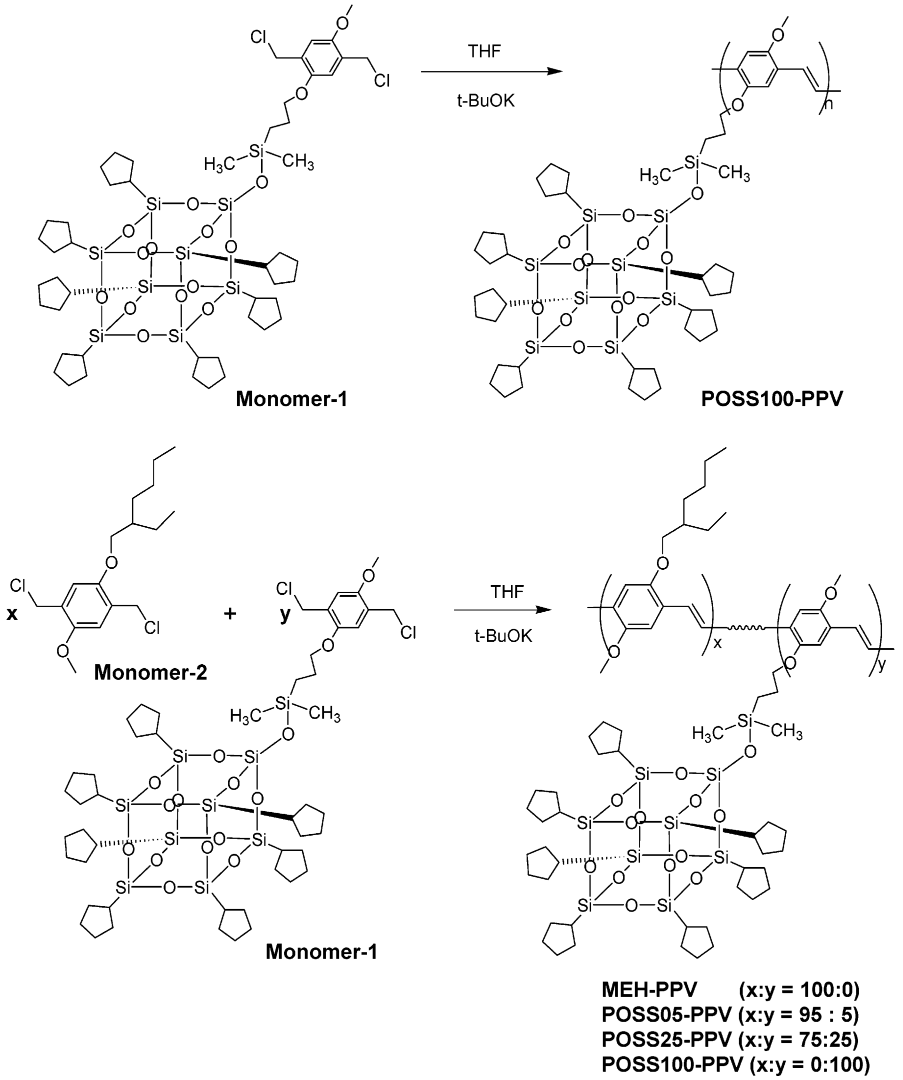


Table 1. Physical Properties of the Polymers

polymer	feed ratio (x:y)	content ratio (x:y)[a]	yield (%)	M_w ($\times 10^4$)	PDI	T_g (°C)	T_d (°C)[b]
MEH-PPV	100/0	100/0	72	1.9	1.20	58	338
POSS05-PPV	95/5	96.3/3.7	69	21.5	3.90	64	330
POSS25-PPV	75/25	81.8/18.2	63	10.8	2.01	70	331
POSS100-PPV	0/100	0/100	45	24.5	5.32	77	305

[a] Content ratios were calculated by NMR-assignment of the polymers, and x:y = number of 2-methoxy-5-ethylhexyloxy-1,4-phenylene units: number of 2-methoxy-5-POSS-1,4-phenylene units. [b] Temp. resulting in 5% weight loss based on initial weight.

from the ratio of the integrals of the ^{1}H NMR spectral features corresponding to O−Si−CH$_x$ (x = 1 or 2) near 0.1 ppm and to aromatic protons.[29] The actual ratios of the POSS-containing monomer units in the polymers were lower than the POSS-containing monomers' feed ratios. This is probably because the bulky POSS units in the POSS-containing monomers prevent the monomer from approaching growing polymer chains.

The thermal properties of the polymers were determined with thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 °C/min. The glass transition temperatures (T_g) were found to increase with increases in the POSS content of the polymers, and the T_g (64−77 °C) values of the POSS-containing polymers were found to be higher than that of MEH-PPV (58 °C).[4] The higher glass transition temperatures of the POSS-containing polymers are attributed to the presence of the robust POSS units on the side chains of the polymers.[29,32] The polymers exhibited good thermal stability, with decomposition temperatures for 5% weight loss (T_d) above 300 °C. The TGA traces of the polymers are shown in Figure 2.

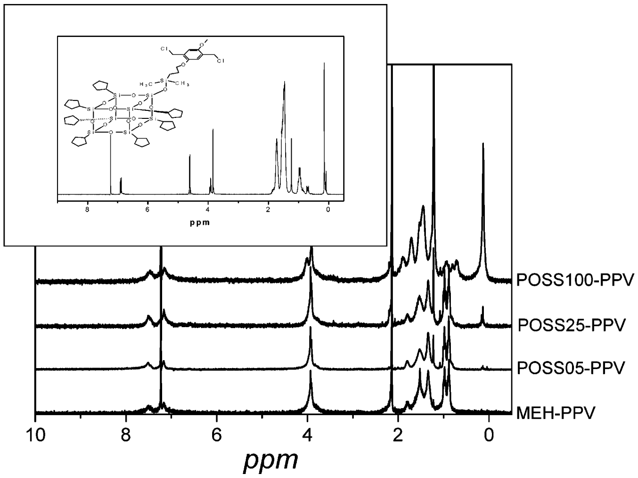


Figure 1. ^{1}H NMR spectra of the Monomer-1 and polymers.

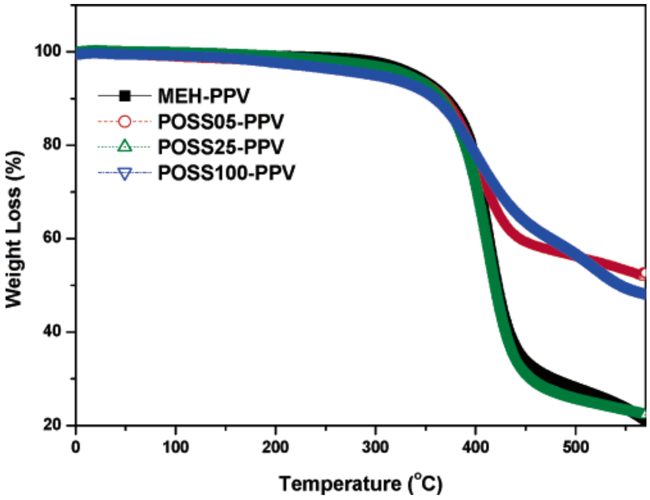


Figure 2. TGA thermograms of the polymers.

Optical and Photoluminescence Properties

The UV−vis absorption and photoluminescence (PL) spectra of the POSS-containing polymers in dilute chloroform solutions are shown in Figure 3. The maximum absorption wavelengths (487−497 nm) and spectral patterns of the polymers in chloroform solution are not significantly different from those of MEH-PPV (maximum absorption wavelength, 493 nm).[29,32] As the POSS content ratio of the polymers increases, the maximum absorption wavelength of the polymers is increasingly blue-shifted.[32] The PL spectra of the polymers in chloroform have a maximum emission wavelength of 548−556 nm for all of the polymers, as shown in Figure 3. As the POSS content ratio of the polymers increases, the maximum emission wavelength of the polymers is also increasingly blue-shifted.[32] The onsets and shapes of the emission spectra of the polymers in chloroform are similar to those of MEH-PPV.[29] From the UV−vis absorption spectra and PL spectra of the polymers, it seems that the introduction of POSS units into the side positions of the PPVs does not significantly alter the electronic structure of MEH-PPV.[32]

The UV−vis absorption and PL spectra of thin films of the POSS-containing polymers on quartz plates are also shown in Figure 3. The UV−vis absorption patterns of the POSS-containing polymers are similar to that of MEH-PPV (an absorption maximum of 498 nm), showing absorption maxima in the range of 491−505 nm. The band gaps of MEH-PPV and the POSS-containing polymers were estimated from the UV−vis absorption edges for the film-state polymers and were found to range from 2.16 to 2.18 eV. The band gaps of the POSS-containing polymers are similar to that of MEH-PPV.[32] The PL spectra of thin films of the POSS-containing polymers have emission maxima at 578−582 nm, which are almost the same as the maximum wavelength of MEH-PPV (581 nm). Furthermore, the onsets and shapes of the polymers are also similar to those of MEH-PPV in its PL spectra.[29] The relative PL quantum yields of the polymers were found to be in the range of 1.17−3.34 and are listed in Table 2. As the POSS content ratio in the POSS-containing PPVs increases, the PL quantum yield of the polymers increases steeply.[32] In particular, POSS100-PPV has the highest relative PL quantum efficiency, 3.34, that is, the

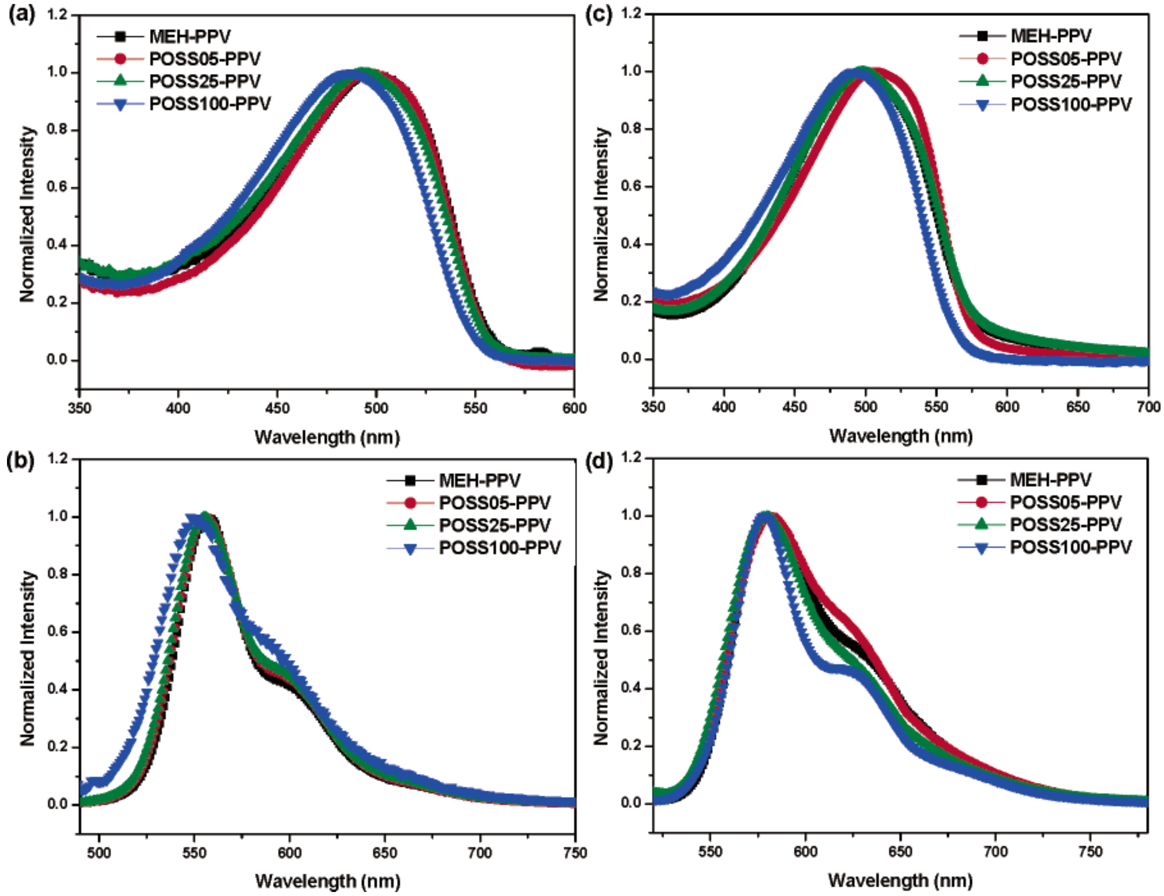


Figure 3. (a) UV−vis absorption spectra of the polymers in $CHCl_3$ solution. (b) PL emission spectra of the polymers in $CHCl_3$ solution. (c) UV−vis absorption spectra of the polymers in the solid state (from $CHCl_3$ solution). (d) PL emission spectra of the polymers in the solid state (from $CHCl_3$ solution).

Table 2. Optical Properties of the Polymers

polymer	λ_{max} (UV, nm) solution	λ_{max} (UV, nm) film	λ_{max} (PL, nm) solution	λ_{max} (PL, nm) film	E_g (eV, UV/nm)[a]	Φ_{PL}[b]
MEH-PPV	493	498	556	581	2.16	1
POSS05-PPV	497	505	556	582	2.16	1.17
POSS25-PPV	492	498	555	580	2.16	1.14
POSS100-PPV	487	491	548	578	2.18	3.34

[a] E_g, calculated from the onset values of the absorption spectra of the spin-coated films on quartz. [b] The film fluorescence quantum yields measured on quartz plates relative to that of MEH-PPV, taken to be 1.00 for comparison (1 wt % in $CHCl_3$).

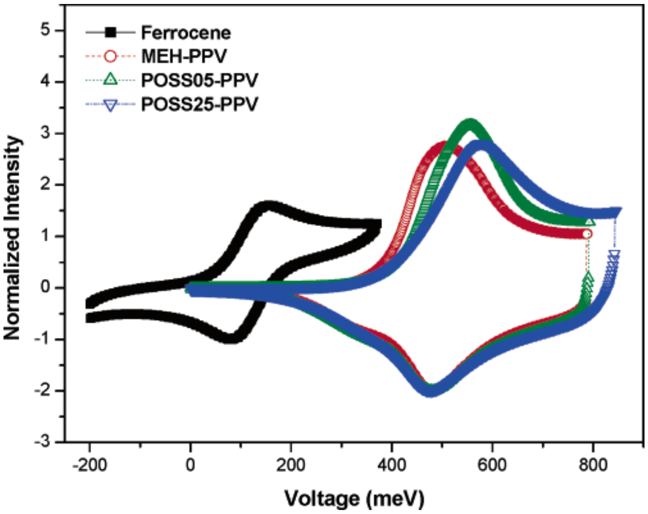


Figure 4. Cyclic voltammograms of the polymers.

Table 3. Electrochemical Properties and Energy Levels of the Polymers

polymer	p-doping (meV vs SCE) E_{pa}	E_{pc}	$E_{1/2}$	E_g (eV, UV/nm)[a]	HOMO (eV)[b]	LUMO (eV)[c]
MEH-PPV	505	487	496	2.16	5.18	3.02
POSS05-PPV	557	482	520	2.16	5.20	3.04
POSS25-PPV	577	479	528	2.16	5.21	3.05
POSS100-PPV	639	455	547	2.18	5.23	3.05

[a] E_g, calculated from the onset values of the absorption spectra of the spin-coated films on quartz. [b] Determined from $E_{1/2}$ (energy level of ferrocene set at 4.8 eV under vacuum). [c] Calculated from HOMO and E_g.

PL quantum efficiency of POSS100-PPV is 3.34 times higher than that of MEH-PPV.

Electrochemical Properties

To investigate the electrochemical properties of the polymers, cyclic voltammetry (CV) measurements were carried out.[15,29] In these electrochemical experiments, a polymer-coated platinum electrode was used as the working electrode, a platinum wire was used as the counter electrode, and an $Ag/AgNO_3$ (0.10 M) electrode was used as the reference electrode. Cyclic voltammetry was performed with the three electrodes immersed in a solution of 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4-NBF_4) in anhydrous acetonitrile at ambient temperature under nitrogen gas with a scan rate of 50 mV/s. After scanning the polymers in the cyclovoltammetric cell, the measurements were calibrated using ferrocene as the oxidation reaction standard. The oxidation waves of ferrocene and the polymers induced by p-type doping are shown in Figure 4. The HOMO energy levels of the polymers were estimated to be in the range of 5.20−5.23 eV from the first oxidation process and are listed in Table 3. The band gap energies of the polymers were determined from the onsets of the UV spectra of the polymers in the solid state, and the LUMO energy levels of the polymers were obtained from the differences between the HOMO energy levels and the band gap energies. The LUMO energy levels of the polymers were found to range from 3.04 to 3.05 eV and are listed in Table 3. The band gap energies of the polymers were found to range from 2.16 to 2.18 eV.[15,32] As shown in Table 3, the POSS-containing PPVs have HOMO and LUMO energy levels and band gap energies similar to those of MEH-PPV, indicating that the presence of the POSS moieties in the PPVs does not result in changes in the electronic structure of the polymers.[15,29,32]

Electroluminescent Properties and Current−Voltage−Luminance (*I*−*V*−*L*) Characteristics

EL devices with the configuration ITO/PEDOT:PSS/polymer/Ca/Al were fabricated for each copolymer to investigate their electroluminescence properties and current−voltage−luminance characteristics. PEDOT:PSS was spun-coated onto an ITO substrate to a film thickness of 30 nm and baked under vacuum at 170 °C for 60 min. Each polymer solution was spun-coated onto such a PEDOT-PSS film; the thicknesses of the films were about 80 nm. Ca and Al were consecutively deposited onto each polymer layer. As shown in Figure 5, the EL spectra of POSS05-PPV, POSS25-PPV, and POSS100-PPV have intense peaks at 577, 575, and 543 nm, respectively. It is known that the EL maximum peaks of PPVs are red-shifted with respect to the PL maximum peaks of PPVs. As the POSS content ratio of the polymers increases, the EL spectra of the polymers have decreasing maximum wavelength values (the EL maximum wavelength of MEH-PPV is 595 nm). This kind of phenomenon was also observed in the PL spectra. The reduced effective conjugation length could be attributed to the increasing POSS ratio. As the nanosized POSS ratio is increased, the chain planarity of the MEH-PPV units is a little bit distorted by the surrounding bulky POSS moiety. So, the effective conjugation length of POSS-PPV is reduced compared with that of MEH-PPV. The CIE (Commission Internationale de L'Eclairage) chromaticity coordinates (*x*, *y*) for the EL spectra of POSS05-

Table 4. Electroluminescence Properties of the Polymers

polymers or polymer blends	λ_{max} (EL, nm)[a]	max. lumi. (cd/m^2)[b]	luminance eff. (cd/A)[c]	turn-on voltage (V)[d]
MEH-PPV	595	3880 (14.8V)	0.075	2.4
POSS05-PPV	577	6070 (14.4V)	0.264	3.6
POSS25-PPV	575	6340 (13.2V)	0.262	3.2
POSS100-PPV	543	150 (12.8V)	0.015	4.4
POSS25-PPV, 5% in MEH-PPV	586	11010 (14.3V)	0.477	2.4
POSS25-PPV, 25% in MEH-PPV	583	10340 (13.2V)	0.462	2.4
POSS100-PPV, 5% in MEH-PPV	580	2090 (13.2V)	0.083	2.0
POSS100-PPV, 10% in MEH-PPV	579	1350 (12.8V)	0.054	2.0
POSS100-PPV, 25% in MEH-PPV	578	400 (13.6V)	0.018	2.0

[a] Maximum wavelength of the EL spectra. [b] Maximum brightness (cd/m^2) and the driving voltage at maximum brightness. [c] Luminance efficiency. [d] Voltage at 1 cd/m^2.

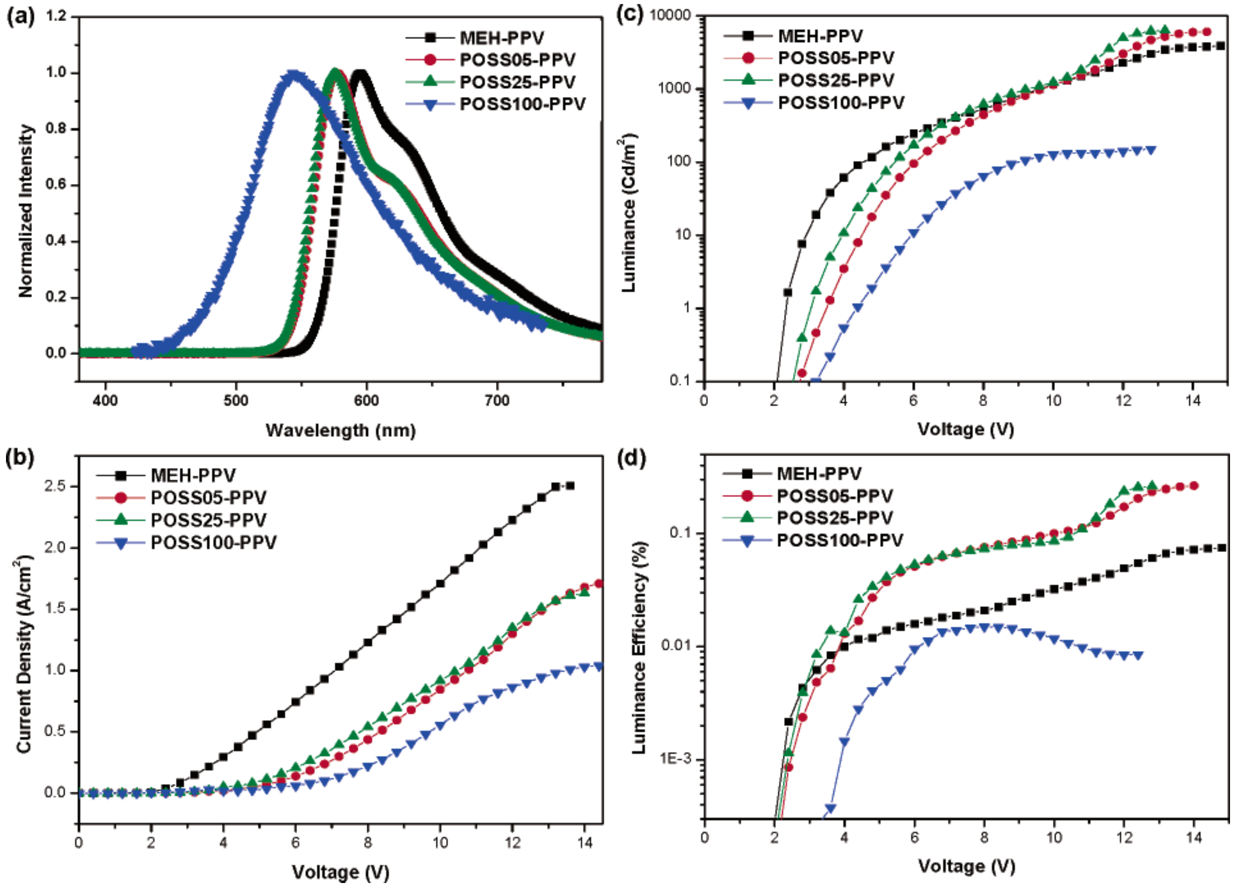


Figure 5. (a) EL spectra of the devices with an ITO/PEDOT:PSS/Polymer/Ca/Al configuration. (b) Voltage−current density ($V-I$) characteristics of the devices. (c) Voltage−luminance ($V-L$) characteristics of the devices. (d) Voltage−luminance efficiency characteristics of the devices.

PPV, POSS25-PPV, and MEH-PPV are (0.55, 0.45), (0.55, 0.45), and (0.57, 0.43), respectively.[32] The EL spectra of POSS05-PPV, POSS25-PPV, and MEH-PPV consist of emissions in the orange-red region, whereas the EL spectrum of POSS100-PPV consists of yellow light emission with CIE coordinates of (0.44, 0.52). The voltage-current density ($V-I$) characteristics of the devices fabricated with the POSS-containing polymers are shown in Figure 5. The turn-on voltages of the POSS05-PPV (3.6 V) and POSS25-PPV (3.2 V) devices are higher than that of the MEH-PPV device (2.4 V). The current densities of the POSS05-PPV and POSS25-PPV devices are lower than that of the MEH-PPV device. The higher turn-on voltages and lower current densities of the POSS05-PPV (3.6 V) and POSS25-PPV (3.2 V) devices can be attributed to the large difference in the energy barrier between PEDOT:PSS and the copolymers. The voltage−luminance ($V-L$) characteristics of the polymers are also shown in Figure 5. The maximum brightness of the POSS05-PPV and POSS25-PPV devices are 6070 cd/m^2 at 14.4 V and 6340 cd/m^2 at 13.2 V, respectively.[32] The brightness maxima of the POSS05-PPV and POSS25-PPV devices are higher than that of the MEH-PPV device (3880 cd/m^2 at 14.8 V). However, the maximum brightness of the POSS100-PPV device is 152 cd/m^2 at 12.8 V. It seems that this extraordinarily low maximum brightness of POSS100-PPV is due to the insulating properties of POSSs in conjugated polymer systems.[29] The luminance efficiencies of the POSS05-PPV and POSS25-PPV devices are in the range of 0.262−0.264 cd/A (Figure 5d), that is, 3.5 times higher than that of MEH-PPV (0.075 cd/A). These results for the $V-I$ and $V-L$ characteristics of the polymers suggest that the introduction of POSSs into PPVs at small molar contents is an easy and efficient method for improving their EL properties such as brightness and quantum efficiency.[29,32]

It has been claimed that blending conjugated polymers and blending a conjugated polymer with a nonconjugated polymer are efficient methods of enhancing the PL and EL efficiencies of polymer-based EL devices.[16,35] We chose POSS25-PPV for blending with MEH-PPV. The EL spectra and $V-L$ curves of blends of POSS25-PPV and MEH-PPV are shown in Figure 6. The luminance efficiencies of the blends are also shown in Figure 6. Surprisingly, the EL efficiencies and brightnesses of blends of MEH-PPV and POSS25-PPV were dramatically enhanced over those of MEH-PPV or the POSS-PPVs. When the POSS25-PPV content ratio of the POSS25-PPV/MEH-PPV blend system is 5 wt %, the maximum wavelength of the EL spectrum is 586 nm. In EL devices, the maximum brightness and maximum luminance efficiency of the blend were found to be 11 010 cd/m^2 and 0.48 cd/A, respectively.[29,32,35] When the POSS25-PPV content ratio of the same blend system was 25 wt % (EL maximum wavelength, 583 nm), the maximum brightness and maximum luminance efficiency were 10 340 cd/m^2 and 0.46 cd/A, respectively. The luminance efficiency of the binary blend consisting of 5 wt % of POSS25-PPV and 95 wt % of MEH-PPV is enhanced by a factor of 6.4. Interestingly, when POSS100-PPV was blended with MEH-PPV, steep decreases in the brightnesses and efficiencies of the EL devices were observed, with increases in the POSS100-PPV content ratio. The voltage−luminance ($V-L$) curves and EL luminance efficiencies of the POSS100-PPV/MEH-PPV blends are shown in Figure 7. It is likely that POSS100-PPV acts as an insulating band with respect to conjugated MEH-PPV, and therefore charge transfer between the conjugated polymer interchains is signifi-

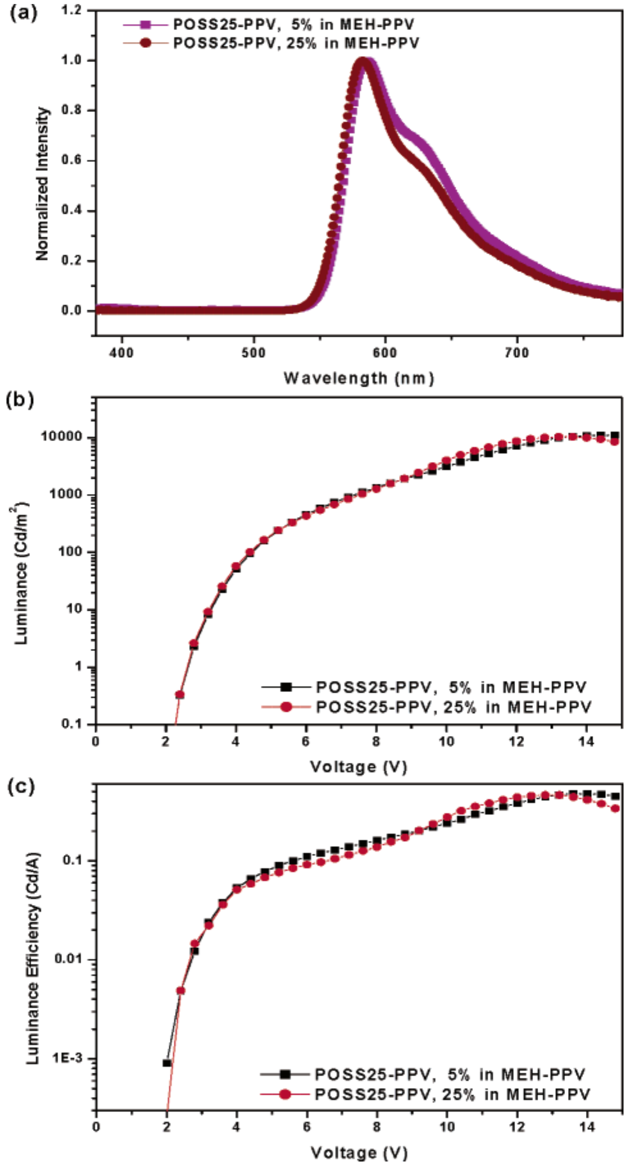


Figure 6. (a) EL spectra of the devices with an ITO/PEDOT:PSS/polymer blends (POSS25-PPV in MEH-PPV)/Ca/Al configuration. (b) Voltage−luminance (*V*−*L*) characteristics of the polymer blends (POSS25-PPV in MEH-PPV). (c) Voltage−luminance efficiency characteristics of the polymer blends (POSS25-PPV in MEH-PPV).

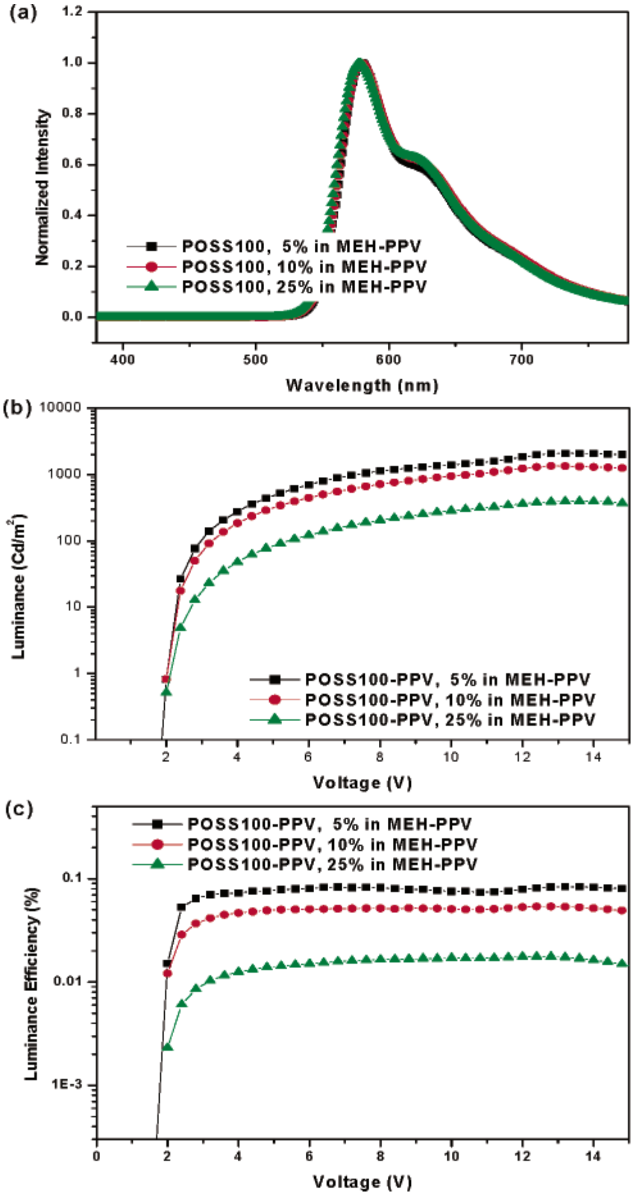


Figure 7. (a) EL spectra of the devices with an ITO/PEDOT:PSS/polymer blend (POSS100-PPV in MEH-PPV)/Ca/Al configuration. (b) Voltage−luminance (*V*−*L*) characteristics of the polymer blends (POSS100-PPV in MEH-PPV). (c) Voltage−luminance efficiency characteristics of the polymer blends (POSS100-PPV in MEH-PPV).

cantly interrupted. From the above results, we reach the following conclusions. The conjugated polymer surrounded partially by insulating POSSs, POSS25-PPV, improves the quantum efficiencies and brightnesses of the EL devices by lowering extraordinarily large hole mobility such that it becomes closer to the electron mobility, thereby balancing the numbers of holes and electrons in the emissive PPV layer.[29,32] In contrast, the conjugated polymer surrounded fully by insulating POSSs, POSS100-PPV, degrades the EL properties by forming an insulating zone and significantly interrupting the transfer of charge carriers in emissive PPVs.

Experimental Section

Measurements and LED Fabrication. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer. UV−visible spectra were recorded on a Shimadzu UV-3100 spectrophotometer with baseline corrections and normalizations carried out using Microsoft Excel software. The molecular weights and polydispersity indices of the polymers were determined by gel permeation chromatography (GPC) analysis relative to a polystyrene standard using a Waters high-pressure GPC assembly Model M590. Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min. The ionization potentials of the polymer films were measured with a low-energy photoelectron spectroscope (Riken-Keiki AC-2). Emission spectra were recorded using dilute ($\sim 10^{-6}$ M) solutions; the spectra were collected on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. 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.[9] 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 chloroform).[9] A Pt wire was used as the counter electrode, and a $Ag/AgNO_3$ (0.10 M in acetonitrile) electrode was used as the reference electrode. EL devices were fabricated as follows. First, a glass substrate was coated with a transparent layer of ITO and then thoroughly cleaned by successive sonication treatments in acetone, isopropyl alcohol, and distilled water. The resulting glass/ITO system was dried with nitrogen gas and then dried by heating at 100 °C. The polymer film was prepared by spin casting a polymer solution containing 0.5 wt % of chloroform. Uniform and pinhole-free films with thicknesses of around 100 nm were obtained easily. Aluminum metal was then deposited on top of the polymer film through a shadow mask by vacuum evaporation at a pressure of less than 4×10^{-6} Torr, yielding active areas of 4 mm^2. For the measurements of device characteristics, current−voltage−luminance (*I*−*V*−*L*) changes were measured using a current/voltage source (Keithley 238), an optical power meter (Newport 818-SL), and a luminance meter (Topcon BM-7). All of the processes and measurements mentioned above were carried out in the open air at room temperature.

Materials. 4-methoxy phenol, allyl bromide, 2-ethylhexyl bromide, 1-(hydridodimethylsilyloxy)-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane, platinum-(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex [Pt(dvs)], 4-*tert*-butylbenzyl bromide, and potassium *t*-butoxide (1.0 M THF solution) were purchased from Aldrich and used without further purification. 1,4-Dioxane, Cerite-545, 37% aqueous formaldehyde, hydrochloric acid, tetrahydrofuran, toluene, anhydrous $MsSO_4$, and sodium hydroxide was purchased from Junsei Chemical Co. Poly-(ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT/PSS) (Bayer), used in LED fabrication, was filtered through a 0.45 μm nylon filter prior to spin coating. The solvents [tetrahydrofuran (THF), dichloromethane and toluene] were freshly distilled and dried following literature methods.

Syntheses of Monomers and Polymers. *Synthesis of 1-Methoxy−4-allyloxy-benzene (**2**).* A solution of 4-methoxy phenol (10 g, 80 mmol) in dry methanol (200 mL) was prepared under an argon atmosphere. To this was added NaOH (4.8 g, 120 mmol), and the mixture was stirred at room temperature under argon for 1 h to ensure complete dissolution. The mixture was refluxed for 20 min, cooled to room temperature, and a solution of allyl bromide (12.6 g, 100 mmol) in dry methanol was added dropwise. The mixture was refluxed under argon for 16 h, during which time the brown solution turned light yellow. The methanol was removed in vacuo and the residue was combined with ether (100 mL). The organic phase was washed with 10% aqueous sodium hydrogen carbonate solution and then with water. The solution was dried over $MgSO_4$ and then filtered off. The solvent was removed in vacuo at 20 °C, and the residue was distilled under reduced pressure to yield the crude title compound as a oil. A pure viscous oil was obtained via column chromatography on silica gel (10 g, yield: 75%). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.34; H, 7.45. ^{1}H NMR ($CDCl_3$, ppm): 3.76 (s, 3H), 4.49 (d, 2H), 5.26−5.45 (m, 2H), 6.02−6.11 (m, 1H), 6.82−6.90 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): 55.5, 69.3, 114.4, 115.6, 117.3, 133.5, 152.6, 153.8.

*Synthesis of 1-Methoxy−4-POSS−benzene (**3**).* A total of 0.84 g (5.2 mmol) of 1-methoxy−4-allyloxy-benzene (compound **2**) and 5 g (5.2 mmol) of hydrido POSS was dissolved in 30 mL of toluene, and 0.1 g of Pt(dvs) solution was dispersed in the solution. The resulting solution was stirred at 80 °C for 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 5.3 g (90%) of the powder product: Anal. Calcd for $C_{47}H_{82}O_{15}Si_9$: C, 49.52; H, 7.25. Found: C, 48.29; H, 7.35. ^{1}H NMR ($CDCl_3$, ppm): 0.13 (s, 6H), 0.62−0.72 (m, 2H), 0.86−1.05 (m, 9H), 1.32−1.81 (m, 56H), 1.83 (t, 2H), 3.75 (s, 3H), 3.84 (t, 2H), 6.80 (s, 4H). ^{13}C NMR ($CDCl_3$, ppm): −0.3, 13.8, 22.3, 23.1, 26.7, 27.0, 56.8, 71.1, 114.6, 115.3, 153.3, 153.6.

Synthesis of 2,5-Bis(chloromethyl)-1-methoxy-4-POSS-benzene (Monomer 1). To a magnetically stirred cooled solution (0−5 °C) of 1-methoxy-4-POSS-benzene (4 g, 3.5 mmol) in 1,4-dioxane (80 mL), we added hydrochloric acid (30 mL) and 37% aqueous formaldehyde (30 mL). Anhydrous HCl gas was bubbled through the stirred, cooled solution (0−5 °C) for 30 min. The reaction mixture was warmed to room temperature and stirred for 16 h. The reaction mixture was then heated to reflux for 4 h. Cooling to room temperature followed by removal of the solvents in vacuo at 25 °C gave an white waxy residue. The residue was combined with ether (100 mL), and the organic phase was washed with water. After the organic phase was dried over $MgSO_4$, the solvent was removed in vacuo at 20 °C. The resulting solid was recrystallized from hexane/methanol by dissolving in the minimum amount of hexane and then adding methanol until the solution became turbid followed by cooling to −23 °C. The title compound was filtered, washed with cold methanol, and dried in vacuo at 20 °C to give a white crystalline solid (3.5 g, yield: 81%) as the solid-state product. Anal. Calcd for $C_{49}H_{84}O_{15}Si_9$: C, 47.58; H, 6.85. Found: C, 47.60; H, 6.92. ^{1}H NMR ($CDCl_3$, ppm): 0.15 (s, 6H), 0.63−0.74 (m, 2H), 0.75−1.08 (m, 9H), 1.33−1.81 (m, 56H), 1.86 (t, 2H), 3.84 (s, 3H), 3.92 (t, 2H), 4.61 (d, 4H), 6.90 (d, 2H). ^{13}C NMR ($CDCl_3$, ppm): −0.3, 13.7, 22.3, 23.1, 27.0, 27.3, 41.3, 56.2, 71.7, 113.2, 114.5, 126.8, 127.1, 150.6, 151.0.

Synthesis of Polymers. *Synthesis of Poly[(2-methoxy-5-POSS-1,4-phenylene)vinylene] (POSS100-PPV).* A solution of 6 mL of potassium *tert*-butoxide (1.0 M THF solution, 4.8 mmol) was added to a stirred solution of monomer 1, 2,5-bis(chloromethyl)-1-methoxy-4-POSS-benzene (1.0 g, 0.8 mmol) in 20 mL of dry THF over 30 min using a syringe pump. The reaction mixture, which exhibited gradually increasing viscosity and orange-red fluorescence, was stirred for 24 h at room temperature. The resulting polymer was sequentially end-capped with a small amount of 4-*tert*-butylbenzyl bromide and then stirred for another hour. The polymerization solution was poured into 600 mL of methanol, and the crude polymer was Soxhlet-extracted successively with methanol, isopropyl alcohol, and hexane to remove the unreacted monomers, impurities, and oligomers, to give a orange-red polymer as a film state (45% yield). Anal. Calcd for POSS100-PPV: C, 50.56; H, 7.10. Found: C, 50.47; H, 6.99. ^{1}H NMR ($CDCl_3$, ppm): 0.13, 0.55−1.05, 1.12−2.07, 2.08−2.46, 3.62−4.25, 6.87−7.83.

Synthesis of POSS05-PPV, POSS25-PPV, and MEH-PPV. POSS05-PPV and POSS25-PPV were prepared according to the above procedures using monomer 1 and monomer 2. MEH-PPV was prepared according to the same procedures using only monomer 2. Anal.Calcd for MEH-PPV: C, 78.42; H, 9.29. Found: C, 78.21; H, 9.30. Anal.Calcd for POSS05-PPV: C, 73.11; H, 8.87. Found: C, 74.14; H, 8.92. Anal. Calcd for POSS25-PPV: C, 61.75; H, 7.98. Found: C, 63.97; H, 8.14. The ^{1}H NMR spectra of POSS05-PPV, POSS25-PPV, and MEH-PPV are similar to that of POSS100-PPV except that the broad peak is not observed near 0.1 ppm in the ^{1}H NMR spectra of MEH-PPV.

Conclusions

We synthesized a new series of POSSs-based PPVs via the Gilch polymerization method. The POSS-containing PPVs were found to have higher glass transition temperatures (64−77 °C) than that of MEH-PPV (58 °C) and good solubility in common organic solvents. As the POSS content ratio of the polymers increases, the maximum wavelengths of the UV−vis absorption and PL emission spectra were increasingly blue-shifted in both solution and solid states except for those of POSS05-PPV. LED devices with ITO/PEDOT:PSS/polymer/Ca/Al configurations were fabricated using the novel POSS-containing PPVs and were found to exhibit maximum EL wavelengths ranging from 577 to 543 nm (POSS05-PPV, 577 nm; POSS25-PPV, 575 nm; and POSS100-PPV, 543 nm). The maximum brightness and luminance efficiency of POSS25-PPV were up to 6340 cd/m^2 at 13.2 V and 0.262 cd/A at 6190 cd/m^2, respectively, which are higher than those of MEH-PPV(3880 cd/m^2 at 14.8 V and 0.075 cd/A at 3880 cd/m^2). Surprisingly, the luminance efficiency (0.48 cd/A at 10 540 cd/m^2) of the binary blend consisting of 5 wt % POSS25-PPV and 95 wt % MEH-PPV was enhanced by a factor of 6.4 compared to that of MEH-PPV, with a maximum brightness of 11 010 cd/m^2 (at 14.3 V). The EL efficiencies of EL devices depend not only on the PL efficiencies of the emitting polymers but also on the charge balance and charge mobility. The fabrication of EL devices with POSS-containing copolymers and even better EL performances is underway.

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