

Highly Efficient Light-Emitting PPV Derivatives Containing Polyhedral Oligomeric Silsesquioxanes (POSSs)

Jong-Min Kang¹, Hoon-Je Cho², Jae-Hoon Eom¹, Jeong-Ik Lee³, Sang-Kyu Lee², Jonghee Lee², Nam-Sung Cho², Hong-Ku Shim^{2*} and Do-Hoon Hwang^{1*}

¹Dept. of Applied Chemistry, Kumoh National Institute of Technology, Kumi 730-701, Korea
TEL:82-54-478-7821, e-mail: dhhwang@kumoh.ac.kr.

²Dept. of Chemistry and School of Molecular Science (BK21), KAIST, Taejon 305-701, Korea

³Basic Research Lab. ETRI, Taejon 305-350, Korea

Keywords : Light-Emitting , PPV Derivatives, Polyhedral Oligomeric Silsesquioxanes

Abstract

A new series of highly bright and efficient poly(*p*-phenylenevinylene)s (PPVs) 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(containing 25 mol % POSS-appended PPV units), and POSS100-PPV(containing 100 mol % POSS-appended PPV units; this is the first π -conjugated polymer composed of 100 mol % POSSs-appended repeating units). 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. Light-emitting diodes (LEDs) with the configuration of ITO/PEDOT:PSS/polymer/Ca/Al were fabricated using the novel POSS-containing PPVs. Surprisingly, the luminescence efficiency (0.48 cd/A at 10540 cd/m²) of the binary blend consisting 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 11010cd/m² (at 14.3 V).

1. 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. π -Conjugated polymers such as poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenylene) (PPP), polythiophene (PT), poly(thienylenevinylene) (PTV), poly(*p*-phenyleneethynylene) (PPE), polyfluorene (PF), and their derivatives 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 [2-4]. However, it is well-known that PPVs are poor electron acceptors because of their high LUMO energy levels, resulting in the difficult electron injection and thus an imbalance in electron and hole injection. In this paper, we 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 a facile and efficient method for improving the brightness and quantum efficiency of EL devices fabricated with PPV derivatives. The chemical structures of the synthesized polymers are illustrated in Figure 1.

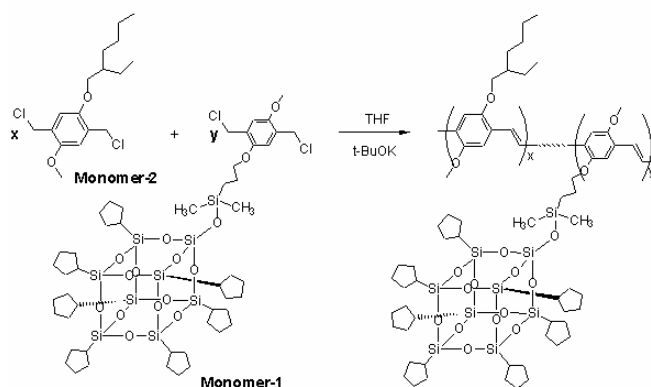


Figure 1. Chemical structure of the POSS containing polymers.

2. Experimental

Measurements and LED fabrication

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% by weight of chloroform. Uniform and pinhole-free films with thicknesses of around 100 nm were easily obtained. 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 mm². 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 processes and measurements mentioned above were carried out in the open air at room temperature.

3. Results and discussion

The UV-vis absorption and photoluminescence (PL) spectra of the POSS-containing polymers in dilute chloroform solutions are shown in Figure 2. 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). As the POSS content ratio of the polymers increases, the maximum absorption wavelength of the polymers is increasingly blue-shifted. The PL spectra of the polymers in chloroform have a maximum emission wavelength of 548–556 nm for all the polymers. As the POSS content ratio of the polymers increases, the maximum emission wavelength of the polymers is also increasingly blue-shifted. The onsets and shapes of the emission spectra of the polymers in chloroform are similar to those of MEH-PPV. 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. The UV-vis absorption patterns of the POSS-containing polymers are similar to that of MEH-PPV ($\lambda_{\text{max}} = 498$ nm),

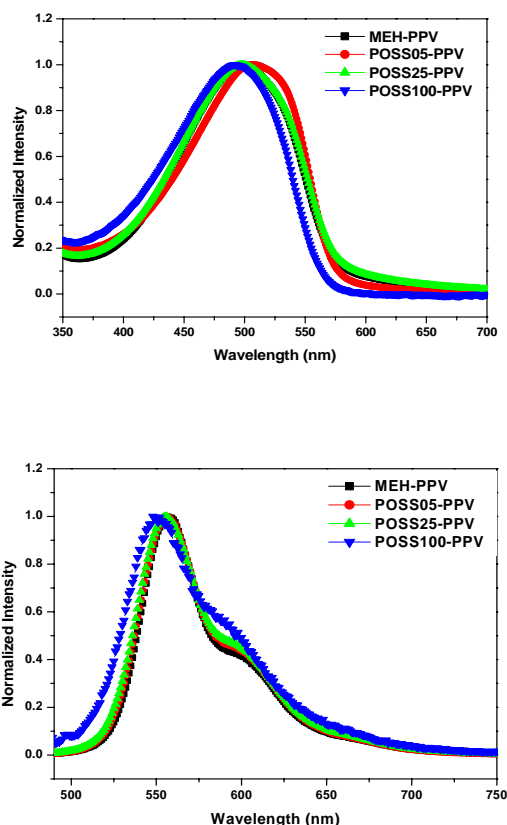


Figure 2. UV-visible (above) and PL (below) spectra of the MEH-PPV and the copolymers.

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 2.16–2.18 eV. The band gaps of the POSS-containing polymers are similar to that of MEH-PPV. 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). Further, the onsets and shapes of the polymers are also similar to those of MEH-PPV in its PL spectra. The relative PL quantum yields of the polymers were found to be in the range of 1.17–3.34. As the POSS content ratio in the POSS-containing PPVs increases, the PL quantum yield of the polymers increases steeply. In particular, POSS100-PPV has the highest relative PL quantum efficiency, 3.34, i.e., the PL quantum efficiency of POSS100-PPV is 3.34 times higher than that of MEH-PPV.

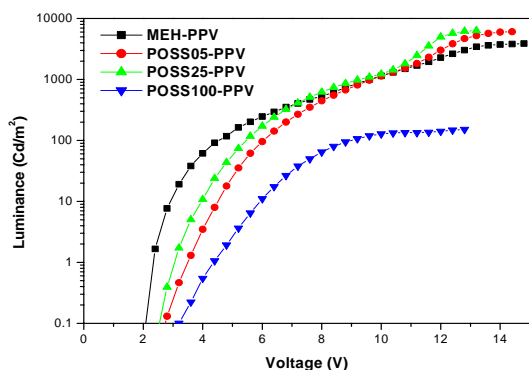


Figure 3. V-L curves of the devices using the polymers.

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 spin-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 spin-coated onto such a PEDOT-PSS film; the thicknesses of the films were about 80nm. Ca and Al were consecutively deposited onto each polymer layer. The EL spectra of POSS05-PPV, POSS25-PPV, and POSS100-PPV have intense peaks at 577 nm, 575 nm, 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 CIE (Commission Internationale de L'Eclairage) chromaticity coordinates (x, y) for the EL spectra of POSS05-PPV, POSS25-PPV, and MEH-PPV are (0.55, 0.45), (0.55, 0.45), and (0.57, 0.43) respectively. 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-luminance (V-L) characteristics of the devices fabricated with the POSS-containing polymers are shown in Figure 3.

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 6073 cd/m² at 14.4 V and 6342 cd/m² at 13.2 V, respectively. The brightness maxima of the POSS05-PPV and POSS25-PPV devices are higher than that of the MEH-PPV device (3879 cd/m² at 14.8 V). However, the maximum brightness of the POSS100-PPV device is 152 cd/m² 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. The luminance efficiencies of the POSS05-PPV and POSS25-PPV devices are in the range of 0.262-0.264 cd/A, i.e., 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.

It has been claimed that blending conjugated polymers and blending a conjugated polymer with a non-conjugated polymer are efficient methods of enhancing the PL and EL efficiencies of polymer-based EL devices. We chose POSS25-PPV for blending with MEH-PPV. Surprisingly, the EL efficiencies and brightness 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 586nm. In EL devices, the maximum brightness and maximum luminance efficiency of the blend were found to be 11,010 cd/m² and 0.48 cd/A, respectively. 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/m² 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

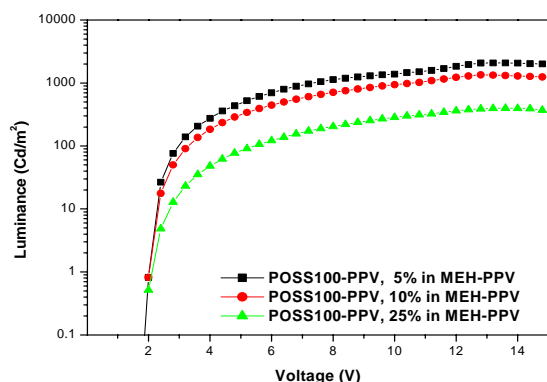


Figure 4. V-L curves of the devices using the polymer blends composed of MEH-PPV and POSS100-PPV.

factor of 6.4. Interestingly, when POSS100-PPV was blended with MEH-PPV, steep decreases in the brightness 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 4.

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 inter-chains is significantly 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 brightness 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. 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.

4. Conclusion

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. Surprisingly, the luminance efficiency (0.48cd/A at 10,540cd/m²) 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 11,010cd/m² (at 14.3V). The EL efficiencies of EL devices depend not only on the PL efficiencies of the emitting polymers but also on the charge balances and charge mobility.

5. Acknowledgements.

The authors gratefully acknowledge the support of the Center for Advanced Functional Polymers (CAFPoly) through KOSEF and BK21 program through the Ministry of Education and Human Resources.

6. References

- [1]. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackey, K.; Friend, R. H.; Burns, P. L.; A. B. Holmes, *Nature* **1990**, 347, 539.
- [2]. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, 397, 121.
- [3] Hwang, D. H.; Kim, S. T.; Shim, H. K.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Chem. Commun.* **1996**, 2241.
- [4]. (a) Ahn, T.; Jang, M. S.; Shim, H. K.; Hwang, D. H.; Zyung, T. *Macromolecules* **1999**, 32, 3279