Electroluminescent Polyhedral Oligomeric Silsesquioxane-Based Nanoparticle

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Received May 2, 2006. Revised Manuscript Received May 31, 2006

A polyhedral oligomeric silsesquioxane (POSS)-based blue light electroluminescent nanoparticle, POSS-FL3, which contains a terfluorene chromophore on each of its eight arms, was easily prepared via the hydrosilation reaction between octakis(dimethylsiloxy)silsesquioxane and an allyl-functionalized terfluorene chromophore that emits blue light as a result of photo- or electroexcitation. POSS-FL3 exhibits good solubility in common organic solvents, such as chloroform, THF, toluene, *p*-xylene, and chlorobenzene, and good film-forming properties on a quartz plate or an indium tin oxide (ITO) plate; i.e., it has good solution processing properties. The good spectral overlap of the maximum absorption wavelength (391 nm in THF solution) of poly(dihexylfluorene) with the maximum emission wavelengths (394 in THF solution) of POSS-FL3 suggests that POSS-FL3 can be used as a dopant of blue light-emissive conjugated polymers such as polyfluorenes to increase their quantum efficiencies through energy transfer. A single-layered electroluminescence (EL) device with the configuration of ITO/PEDOT:PSS/POSS-FL3/Ca (500 nm)/Al (800 nm) was fabricated, with maximum EL peaks at 400, 422, and 464 nm. The external quantum efficiency (EQE) of the POSS-FL3 device (0.0164%) was found to be higher than that of poly-(dihexylfluorene) devices in EL devices (0.0095%). Surprisingly, the external quantum efficiencies in EL devices of POSS-FL3 doped poly(dihexylfluorene) blends were found to be about 4−8 times greater than that of poly(dihexylfluorene).

Introduction

Polyhedral oligomeric silsesquioxanes (POSSs) are well-known hybrid organic−inorganic structures that have unique nanosize applications such as in nanoblocks and nanopores.[1−3] Each POSS unit is a cube-shaped nanoparticle in which the inorganic core is surrounded by eight organic functional groups.[3,4] POSS units have recently received considerable interest due to the improvements they offer in quantum efficiencies and the suppression of aggregation in photoluminescence (PL) and electroluminescence (EL) studies of conjugated polymers such as polyfluorenes and poly(*p*-phenylenevinylene)s.[5−7] Furthermore, the use of POSS units as nanocomposites or nanoparticles in EL devices has been explored.[8−10] Laine et al. has demonstrated the syntheses of octa(aminophenyl)silsesquioxane from trichlorophenylsilane[8] and FL03-OVS from octavinylsilsesquioxane (OVS), explored the application of FL03-OVS as a hole-transporting

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nanocomposite in electroluminescent devices,[9] and also successfully demonstrated the syntheses of robust polyaromatic octasilsesquioxanes from polybromophenylsilsesquioxanes and the enhanced PL emissive properties of F_xOPS (one of six polyaromatic octasilsesquioxanes) with respect to those of poly(dialkylfluorene).[10] He et al. has reported the syntheses of highly efficient luminescent polyaromatic octasilsesquioxanes, in which biphenyl or terphenyl moieties are attached to POSS cores, and also demonstrated the syntheses and optical properties of polyaromatic octasilsesquioxanes containing tetraphenyl moieties as the chromophores.[11] Kawakami et al. reported a fully carbazole-substituted POSS and the enhancement of its PL properties over those of poly(9-vinylcarbazole).[12] Despite the various applications of POSS units as nanocomposites or nanoparticles in EL devices reported by these research groups,[8−12] electroluminescent POSS-based nanoparticles emitting visible light have not previously been demonstrated.[13]

We report here the synthesis and electroluminescence properties of the first POSS-based blue-light (visible-ray range) electroluminescent nanoparticle, POSS-FL3.[14] In this paper, it is shown that POSS-FL3 based on POSS and fluorene moieties is a blue light-emitting nanoparticle, that is, it acts as a good dopant because of the transfer of its excitation energy to blue light-emitting poly(dialkylfluorene),[14,15] and therefore that it can be used to improve the quantum efficiency of poly(dialkylfluorene) in POSS-FL3/poly(dialkylfluorene) blend systems.[15]

Experimental Section

Measurements and LED Fabrication. The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer. The UV−visible spectra were recorded on a Shimadzu UV-3100 spectrophotometer, and baseline corrections and normalizations were carried out using Microsoft Excel software. The molecular weights and polydispersity indices of the polymers were determined with gel permeation chromatography (GPC) analysis relative to a polystyrene standard by a Waters high-pressure GPC assembly Model M590. The thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min. Photoluminescence excitation and 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 using 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. SEM images were obtained with a field emission Philips SEM-535M microscope operating at 10 kV. The POSS-FL3 sample was coated with gold before the SEM investigation. The 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 blend and POSS-FL3 films were prepared by spin casting the polymer blend and POSS-FL3 solutions containing 1.0−3.0 wt % of chloronbenzene. Uniform films with thicknesses of around 30 and 100 nm were easily obtained for POSS-FL3 and polymer blends, respectively. The metals Ca and Al were consecutively deposited onto the polymer blend and POSS-FL3 films through a shadow mask by vacuum evaporation at a pressure of $<4 \times 10^{-6}$ 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 processes and measurements mentioned above were carried out in open air at room temperature.

Materials. 2-Bromofluorene, 2,7-dibromofluorene, 1-bromobutane, 1-bromohexane, 2-(2-bromoethoxy)tetrahydro-*2H*-pyran, tetrabutylammonium bromide (TBAB), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, tetrakis(triphenylphosphine)palladium, *tert*-butyllithium, allyl bromide, 1,3,5,7,9,11,13,15-octakis(dimethylsilyloxy)pentacyclo-[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)], Aliquat-336$^{@}$, and chlorobenzene were purchased from Aldrich Chem. Com. Inc. and used without further purification. Cerite-545, 35% aqueous hydrochloric acid, chloroform, ethyl acetate, tetrahydrofuran, toluene, anhydrous magnesium sulfate ($MgSO_4$), potassium carbonate (K_2CO_3), and sodium hydroxide (NaOH) were purchased from Junsei Chemical Co. Poly(ethylenedioxythiophene)−poly(styrenesulfonate) (PEDOT:PSS) (from Bayer), used in the LED fabrication, was filtered through a 0.45 μm nylon filter prior to spin coating. Tetrahydrofuran (THF) was freshly distilled and other organic solvents were used without further purification.

Syntheses of Materials. *Synthesis of 2-Bromo-9,9-dibutyl-9H-fluorene (**2**).* To a solution of 12.3 g (50.0 mmol) of 2-bromofluorene, 16.4 g (120.0 mmol) of 1-bromobutane, 30 mL of toluene, and 1.20 g of tetrabutylammonium bromide as a phase-transfer catalyst was added 80 mL of a 50 wt % sodium hydroxide aqueous solution. The reaction mixture was refluxed at 80 °C for 12 h and then cooled to room temperature. The reaction mixture was extracted with 200 mL of ethyl acetate from saturated aqueous sodium hydrogen carbonate solution, washed with water, dried over anhydrous magnesium sulfate, and then concentrated in vacuo with a rotary evaporator. The crude product was recrystallized from *n*-hexane and then chomatographed on silica gel with a mixture of ethyl acetate and *n*-hexane (1/30) as the eluent, giving 11.6 g of the title product as a white solid: ^{1}H NMR ($CDCl_3$): δ 0.58 (m, 4H), 0.67 (t, 6H), 1.06 (q, 4H), 1.93 (q, 4H), 7.32 (m, 3H), 7.45

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(m, 2H), 7.54 (d, 1H), 7.67 (d, 1H). ^{13}C NMR (CDCl$_3$, ppm): 13.7, 23.0, 25.8, 40.1, 55.3, 119.0, 120.9, 121.0, 122.8, 126.1, 126.9, 127.5 129.9, 140.0, 140.1, 150.3, 152.9. Anal. Calcd for $C_{21}H_{25}Br$: C, 70.59; H, 7.05. Found: C, 70.52; H, 7.03.

Synthesis of 2-(9,9-Dibutyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (*3*). To a solution at −78 °C of 10.7 g (30.0 mmol) of 2-bromo-9,9-dibutyl-9*H*-fluorene in 40 mL of THF at −78 °C was added 35.3 mL (60.0 mmol) of *tert*-butyllithium (1.7 M in hexane) dropwise. The reaction solution was stirred at −78 °C for 2 h, and then 9.44 mL (45.5 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added to the reaction solution. The reaction mixture was stirred at −78 °C for 2 h and then stirred at ambient temperature for 24 h. The reaction mixture was extracted with 200 mL of chloroform from saturated aqueous sodium hydrogen carbonate solution, washed with water, dried over anhydrous magnesium sulfate, and then concentrated in vacuo with a rotary evaporator. The crude product was purified by reprecipitation in hexane and then chromatographed on silica gel with a mixture of ethyl acetate and *n*-hexane (1/10) as the eluent, giving 8.45 g of the title product as a white solid: ^{1}H NMR (CDCl$_3$): δ 0.54 (m, 4H), 0.63 (t, 6H), 1.03 (q, 4H), 1.37 (s, 12H), 1.97 (m, 4H), 7.30 (m, 3H), 7.68 (d, 1H), 7.71 (d, 2H), 7.78 (d, 1H). ^{13}C NMR (CDCl$_3$, ppm): 13.8, 23.0, 24.9, 25.9, 40.1, 55.0, 83.7, 118.9, 120.1, 122.9, 126.6, 126.8, 127.5, 128.8, 133.7, 140.9, 144.1, 149.8, 151.8. Anal. Calcd for $C_{27}H_{37}BO_2$: C, 80.19; H, 9.22. Found: C, 79.97; H, 9.17.

Synthesis of 2-[2-(2,7-Dibromo-9-hexyl-9*H*-fluoren-9-yl)-ethoxy]-tetrahydro-2H-pyran (*5*). To a solution at 80 °C of 14.6 g (45.5 mmol) of 2,7-dibromofluorene, 6.0 g (36.0 mmol) of 1-bromohexane, 12.2 g (58.5 mmol) of 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, 30 mL of toluene, and 1.2 g of tetrabutylammonium bromide as a phase-transfer catalyst was added 100 mL of a 50 wt % sodium hydroxide aqueous solution. The reaction mixture was refluxed at 80 °C for 12 h and then cooled to room temperature. The reaction mixture was extracted with 200 mL of ethyl acetate from saturated aqueous sodium hydrogen carbonate solution, washed with water, dried over anhydrous magnesium sulfate, and then concentrated in vacuo with a rotary evaporator. The crude product was chromatographed on silica gel with a mixture of ethyl acetate and *n*-hexane (1/10) as the eluent, giving 13.0 g of the title product in a viscous oily state: ^{1}H NMR (CDCl$_3$): δ 0.58 (br s, 2H), 0.74 (t, 3H), 0.98−1.18 (m, 6H), 1.20−1.65 (m, 6H), 1.92 (m, 2H), 2.32 (t, 2H), 2.73−3.15 (m, 2H), 3.23−3.47 (m, 2H), 4.10 (t, 1H), 7.41−7.50 (m, 6H). ^{13}C NMR (CDCl$_3$, ppm): 13.9, 19.3, 22.5, 23.3, 25.3, 29.4, 30.4, 31.4, 39.4, 40.7, 53.9, 61.9, 63.6, 98.7, 121.2, 121.5, 126.5, 130.4, 138.9, 151.7. Anal. Calcd for $C_{26}H_{32}Br_2O_2$: C, 58.22; H, 6.01. Found: C, 58.34; H, 6.17.

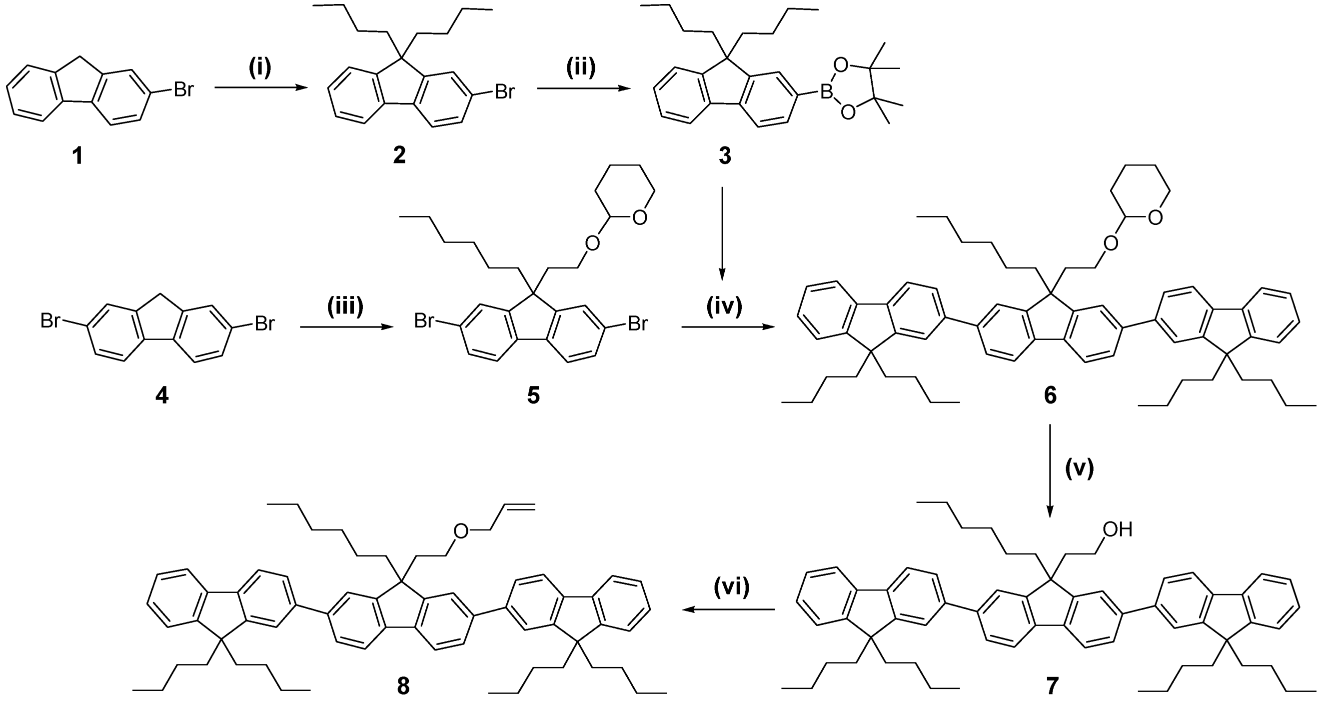
Synthesis of 2-[2-(9,9,9″,9″-Tetrabutyl-9′-hexyl-9*H*,9′*H*,9″*H*-[2,2′;7′,2″]terfluoren-9′-yl)-ethoxy]-tetrahydro-2H-pyran (*6*). Tetrakis(triphenylphosphine)palladium (0.10 g), the air-sensitive Pd(0) catalyst, was inserted into a two-necked 100 mL round bottom flask in a drybox. To the reactor was added a mixture of 3.21 g (6.00 mmol) of 2-[2-(2,7-dibromo-9-hexyl-9*H*-fluoren-9-yl)-ethoxy]-tetrahydro-2*H*-pyran, 7.28 g (18.0 mmol) of 2-(9,9-dibutyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane, and 30 mL of toluene. After 0.20 g of Aliquat 336 as a phase-transfer catalyst and 20.0 mL of 2 M aqueous sodium carbonate solution had been added to the reaction mixture, the reaction solution was stirred at 80 °C for 48 h. The reaction mixture was extracted with 100 mL of chloroform from saturated aqueous sodium hydrogen carbonate solution, washed with water, dried over anhydrous magnesium sulfate, and then filtered through a Buchner funnel. The mother liquor was concentrated in vacuo with a rotary evaporator, and the crude solid product was chromatographed on silica gel with a mixture of ethyl acetate and *n*-hexane (1/30) as the eluent, giving 3.76 g of the title product as a white solid: ^{1}H NMR (CDCl$_3$): δ 0.59−1.04 (m, 25H), 1.04−1.30 (m, 14H), 1.30−1.77 (m, 6H), 1.98−2.30 (m, 10H), 2.67 (t, 2H), 2.92−3.69 (m, 4H), 4.25 (t, 1H), 7.29−7.50 (m, 6H), 7.65−7.93 (m, 14H). ^{13}C NMR (CDCl$_3$, ppm): 13.7, 13.9, 19.5, 22.4, 23.0, 24.9, 25.2, 26.0, 29.5, 30.5, 31.4, 39.6, 40.2, 41.0, 53.4, 55.1, 62.2, 64.3, 99.2, 119.7, 119.8, 120.0, 121.2, 121.3, 122.8, 126.0, 126.4, 126.7, 127.0, 139.7, 140.3, 140.5, 140.7, 140.8, 150.8, 150.9, 151.4. Anal. Calcd for $C_{68}H_{82}O_2$: C, 87.69; H, 8.87. Found: C, 87.34; H, 8.81.

Synthesis of 2-(9,9,9″,9″-Tetrabutyl-9′-hexyl-9H,9′H,9″H-[2,2′;7′,2″]terfluoren-9′-yl)-ethanol (*7*). To a solution of 3.26 g (3.50 mmol) of 2-[2-(9,9,9″,9″-tetrabutyl-9′-hexyl-9*H*,9′*H*,9″*H*-[2,2′;7′,2″]terfluoren-9′-yl)-ethoxy]-tetrahydro-2*H*-pyran was added 50 mL of acidified ethanol (containing 5 mL of a 10 wt % aqueous HCl solution). The reaction mixture was refluxed at 90 °C for 1 h and cooled to room temperature, and then the ethanol in the reaction mixture was evaporated in vacuo. The reaction mixture was extracted with 100 mL of chloroform from a saturated aqueous sodium hydrogen carbonate solution, washed with water, dried over anhydrous magnesium sulfate, and then concentrated in vacuo with a rotary evaporator. The crude product was column chomatographed on silica gel using a mixture of ethyl acetate and *n*-hexane (1/10) as the eluent, giving 2.25 g of the title product as a white solid: ^{1}H NMR (CDCl$_3$): δ 0.66−1.04 (m, 25H), 1.09−1.25 (m, 14H), 2.03−2.33 (m, 10H), 2.60 (t, 2H), 3.25 (t, 2H), 7.32−7.50 (m, 6H), 7.66−7.95 (m, 14H). ^{13}C NMR (CDCl$_3$, ppm): 13.8, 14.3, 22.5, 23.1, 23.4, 25.9, 29.6, 31.4, 40.3, 40.8, 42.8, 53.5, 55.1, 59.5, 119.6, 119.8, 120.4, 121.3, 121.7, 122.4, 126.0, 126.4, 126.6, 126.8, 139.6, 140.1, 140.3, 140.7, 140.8, 150.7, 150.9, 151.5. Anal. Calcd for $C_{63}H_{74}O$: C, 89.31; H, 8.80. Found: C, 89.06; H, 8.67.

Synthesis of 9′-(2-Allyloxy-ethyl)-9,9,9″,9″-tetrabutyl-9′-hexyl-9H,9′H,9″H-[2,2′;7′,2″]terfluorene (*8*). To a solution of 2.12 g (2.50 mmol) of 2-(9,9,9″,9″-tetrabutyl-9′-hexyl-9*H*,9′*H*,9″*H*-[2,2′;7′,2″]terfluoren-9′-yl)-ethanol, 0.605 g (5.00 mmol) of allyl bromide, 20 mL of toluene, and 0.2 g of tetrabutylammonium bromide as a phase-transfer catalyst was added 40 mL of a 50 wt % sodium hydroxide aqueous solution. The reaction mixture was refluxed at 80 °C for 8 h and then cooled to room temperature. The reaction mixture was extracted with 200 mL of chloroform from a saturated aqueous sodium hydrogen carbonate solution, washed with water, dried over anhydrous magnesium sulfate, and then concentrated in vacuo with a rotary evaporator. The crude product was column chromatographed on silica gel with a mixture of ethyl acetate and *n*-hexane (1/30) as the eluent, giving 1.90 g of the title product as a white solid: ^{1}H NMR (CDCl$_3$): δ 0.57−0.93 (m, 25H), 0.99−1.23 (m, 14H), 1.95−2.20 (m, 10H), 2.53 (t, 2H), 2.94 (t, 2H), 3.67 (d, 2H), 4.96−5.15 (m, 2H), 5.63−5.80 (m, 1H), 7.28−7.42 (m, 6H), 7.57−7.86 (m, 14H). ^{13}C NMR (CDCl$_3$, ppm): 13.6, 13.8, 22.8, 23.0, 23.2, 25.8, 28.8, 29.4, 31.3, 40.2, 40.7, 53.2, 55.0, 66.7, 71.5, 116.5, 119.7, 119.8, 120.0, 121.2, 121.5, 122.8, 125.9, 126.3, 126.7, 127.0, 134.5, 139.5, 140.2, 140.3, 140.6, 140.7, 150.7, 150.8, 151.4. Anal. Calcd for $C_{66}H_{78}O$: C, 89.34; H, 8.86. Found: C, 89.11; H, 8.75.

Synthesis of POSS-FL3 (*10*). A total of 0.80 g (0.90 mmol) of 9′-(2-allyloxy-ethyl)-9,9,9″,9″-tetrabutyl-9′-hexyl-9*H*,9′*H*,9″*H*-[2,2′;7′,2″]terfluorene and 0.10 g (0.10 mmol) of octa(hydridosiloxane-functionalized)silsesquioxane, 1,3,5,7,9,11,13,15-octakis-(dimethylsilyloxy)pentacyclo-[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]octasiloxane, was dissolved in 20 mL of toluene, and 0.2 g of Pt catalyst, platinum-(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex [Pt(dvs)], solution was added to the reaction solution. The reaction mixture was stirred at 80 °C for 24 h and then cooled to room temperature. The reaction mixture was concentrated in vacuo with a rotary

Scheme 1. Synthetic Route for 9′-(2-Allyloxy-ethyl)-9,9,9″,9″-tetrabutyl-9′-hexyl-9*H*,9′*H*,9″*H*-[2,2′;7′,2″]terfluorene (8)[a]



[a] (i) 1-Bromobutane, TBAB, NaOH (50 wt % aqueous solution), toluene, 80 °C, 12 h; (ii) *tert*-butyllithium, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, −78 °C, 12 h, and then, 10 °C, 24 h; (iii) 1-bromohexane, 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, TBAB, NaOH (50 wt % aqueous solution), toluene, 80 °C, 12 h; (iv) tetrakis(triphenylphosphine)palladium, Aliquat 336, 2 M Na_2CO_3 (aq), toluene, 80 °C, 48 h; (v) HCl (aq), ethanol, 90 °C, 1 h; (vi) allyl bromide, TBAB, NaOH (50 wt % aqueous solution), toluene, 80 °C, 8 h.

evaporator, and then the crude product was column chromatographed on silica gel with a mixture of ethyl acetate and *n*-hexane (1/10) as the eluent. The product was finally purified with a dialysis method and dried in vacuo, giving 0.62 g of the title product as a brittle white solid: ^{1}H NMR (CDCl_3): δ −0.24 to 0.20 (s, 48H), 0.20−0.52 (d, 16H), 0.52−0.95 (s, 200H), 0.95−1.49 (t, 128H), 1.89−2.24 (d, 80H), 2.39−2.61 (t, 16H), 2.73−3.06 (t, 16H), 3.07−3.25 (t, 16H), 7.21−7.44(m, 48H), 7.50−7.89 (m, 112H). ^{13}C NMR (CDCl_3, ppm): −0.5, 9.1, 13.7, 14.0, 22.5, 22.9, 23.1, 26.1, 29.6, 31.4, 39.7, 40.3, 40.8, 43.0, 53.3, 55.2, 67.1, 73.6, 119.8, 119.9, 120.0, 121.3, 121.4, 123.0, 126.1, 126.4, 126.8, 127.1, 139.6, 140.3, 140.5, 140.7, 140.8, 151.0, 151.5, 151.6. Anal. Calcd for $\text{C}_{544}\text{H}_{672}\text{O}_{28}\text{Si}_{16}$: C, 80.58; H, 8.35. Found: C, 80.15; H, 8.17.

Results and Discussion

The electroluminescent nanoparticle was synthesized via the hydrosilation between octakis(dimethylsiloxy)silsesquioxane and an allyl-functionalized terfluorene chromophore that emits blue light as a result of photo- or electroexcitation.[6,12,16] The molecular structures and synthetic procedures for the chromophore-containing POSSs are shown in Schemes 1 and 2.[16] Compounds **2** and **5** were synthesized by carrying out the alkylation under strong basic conditions of **1** and **4**, respectively.[16] As we reported previously,[16] compound **5** is a useful intermediate in the synthesis of monofunctional fluorene moieties.[6c] Compound **3** was prepared by the addition of a dioxaborolane after activation of **2** with *t*-BuLi.[17] Compound **6** was prepared by using the Suzuki coupling reaction between **3** and **5**.[17] Compound **6** was deprotected in an acidic alcohol solution and then allylated to afford **8**.[16] POSS-FL3, the POSS-based blue light-emitting nanoparticle (compound **10**), was synthesized via the hydrosilation between octakis(dimethylsiloxy)silsesquioxane and an allyl-functionalized terfluorene, compound **8,** under Pt catalysis.[6,12,16] The molecular structures of all the synthesized compounds were confirmed with ^{1}H NMR and ^{13}C NMR spectroscopy and elemental analysis;[6,16] i.e., the results were consistent with the structures of the molecules shown in Schemes 1 and 2. The ^{1}H NMR spectra of compound **8** and POSS-FL3 (**10**) are shown in the Supporting Information. Conventional proton peaks due to the methylene group adjacent to the $-\text{OSi}(\text{CH}_3)_2-$ group were observed near 0.5 ppm for POSS-FL3, and the conventional proton and carbon peaks due to the methyl groups appended to the Si atoms of the −OSi and $-\text{O}_3\text{Si}$ units were observed near 0 ppm in the ^{1}H NMR and ^{13}C NMR spectra.[6,16] POSS-FL3 was found to exhibit very good solubilities in common organic solvents such as methylene chloride, chloroform, THF, toluene, *p*-xylene, and chlorobenzene. Furthermore, films of POSS-FL3 were easily formed when solutions of POSS-FL3 in chloroform or THF were cast onto a glass substrate or an indium tin oxide (ITO) plate, showing that POSS-FL3 is a solution processable electroluminescent nanoparticle that can be used in LED applications. The molecular weight of POSS-FL3 was determined with gel permeation chromatography (GPC) against polystyrene standards with tetrahydrofuran (THF) as the eluent. The number average molecular weight and weight average molecular weight of POSS-FL3 were found to be 6000 and 6400, respectively, giving a polydispersity index of 1.07. It is likely that the discrepancy between

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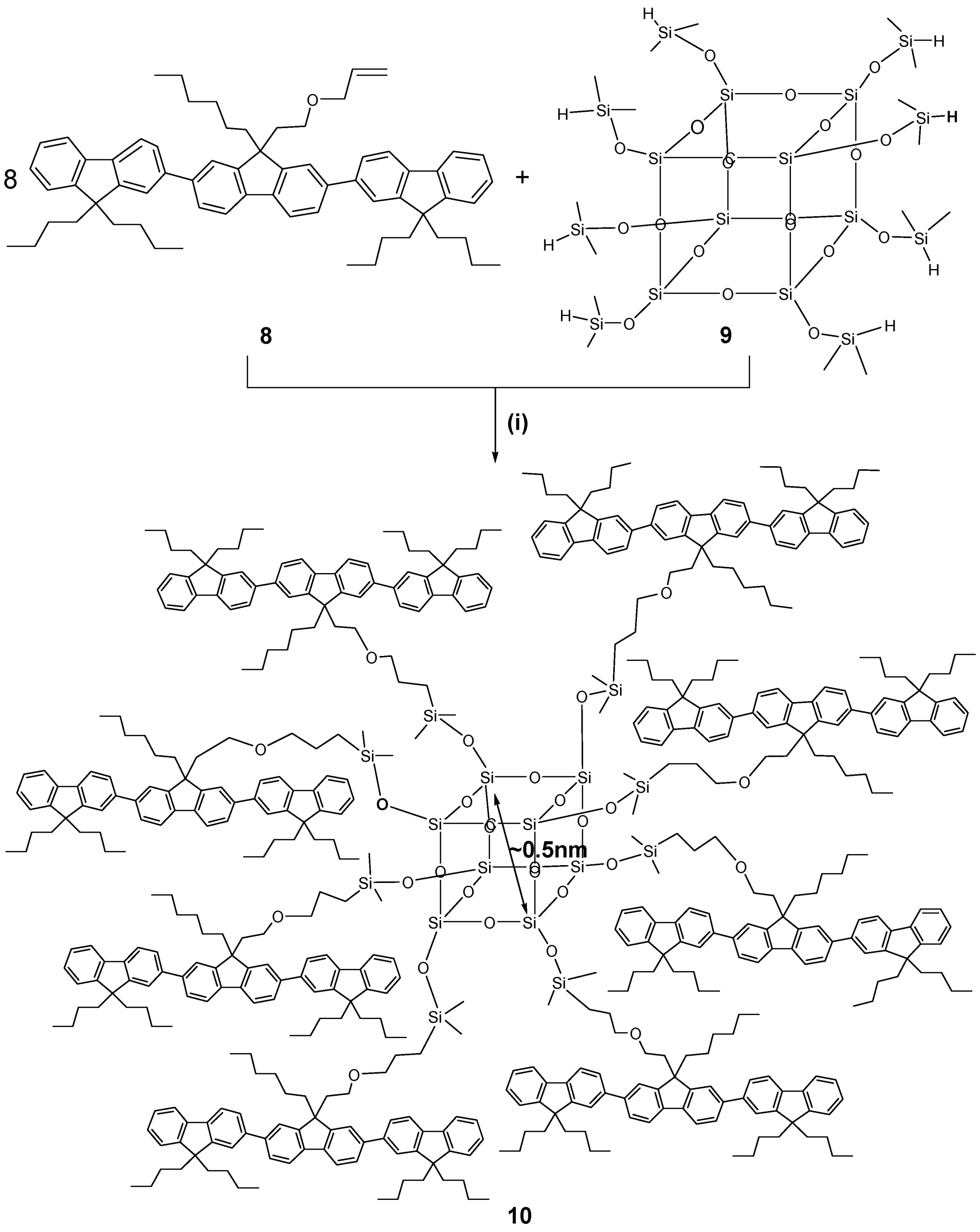
(16) Cho, H. J.; Jung, B. J.; Lee, J.; Cho, N. S.; Shim, H. K. *Macromolecules* **2003**, *36*, 6704.

(17) Lee, J.; Jung, B. J.; Lee, S. K.; Lee, J. I.; Cho, H. J.; Shim, H. K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1845.

Scheme 2. Synthetic Route for POSS-FL3 (10)[a]



[a] (i) Pt(dvs), toluene, 80 °C, 24 h.

the molecular weight (~6000) obtained by GPC analysis and the calculated molecular weight (~8100) of POSS-FL3, which has eight terfluorene moieties on its eight arms, was due to the structural difference between the linear polystyrenes used as the standards in the GPC analysis and the spherical POSS-FL3. The glass transition temperature (T_g) of POSS-FL3 was determined with differential scanning calorimetry (DSC) and found to be 74 °C; this value is higher than that of POSS-Cz ($T_g \sim 37$ °C), which contains a flexible spacer between the POSS core and the appended carbazole units that is similar to that in POSS-FL3.[12] The thermal stability of POSS-FL3 was measured with thermal gravimetric analysis (TGA); POSS-FL3 was found to have a high thermal stability, 5% weight loss over 379 °C.[10] The DSC thermogram and TGA traces of POSS-FL3 (**10**) are shown in the Supporting Information.

The UV−vis and photoluminescence (PL) spectra of POSS-FL3 in chloroform are shown in Figure 1a. The maximum absorption wavelength of POSS-FL3 in THF was found to be 352 nm, with the maxima in the PL emission of POSS-FL3 in THF at 394 and 415 nm. As shown in Figure 1a, the shape of the PL emission spectrum of POSS-FL3 in THF is similar to that of poly(dihexylfluorene),[16,18] and the emission wavelengths of POSS-FL3 are about 20 nm blue-shifted with respect to those of poly(dihexylfluorene) due to the short conjugation length of the terfluorene unit in POSS-FL3 (Figure 3).[18] The maximum absorption wavelength (391 nm) of poly(dihexylfluorene) in THF solution coincides with the maximum emission wavelength (394 nm) of POSS-FL3 in THF solution, and therefore efficient energy transfer from POSS-FL3 to poly(dihexylfluorene) is expected.[15] The UV−vis and PL spectra of POSS-FL3 in the

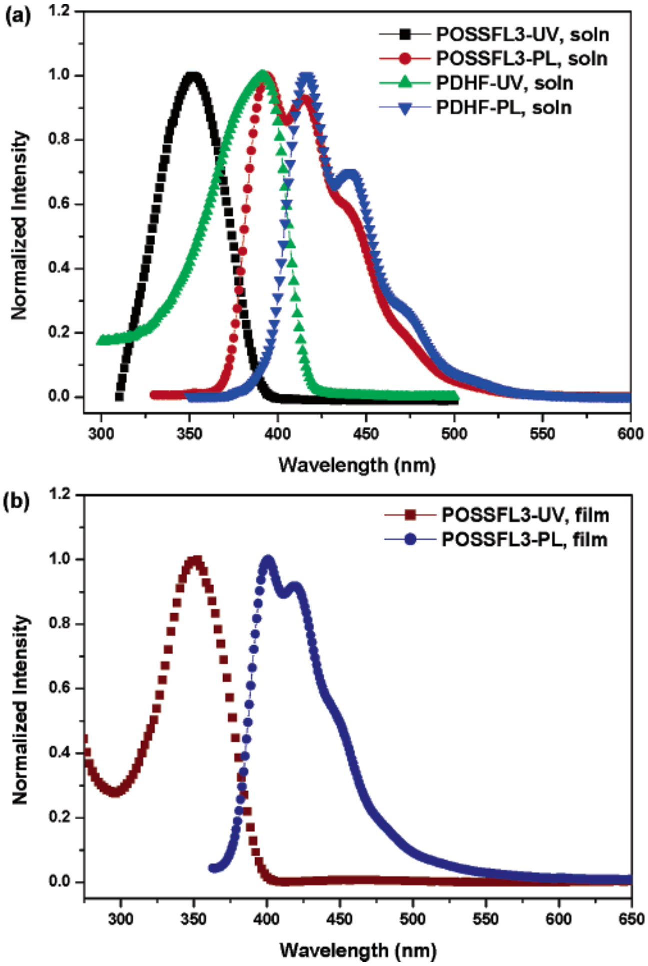


Figure 1. (a) UV−vis absorption and PL emission spectra of POSS-FL3 and poly(dihexylfluorene) (PDHF) in THF solution. (b) UV−vis absorption and PL emission spectra of POSS-FL3 in the solid state.

solid state are also shown in Figure 1b; the maximum absorption wavelength and the maxima in the PL emission of POSS-FL3 in the solid state are 353 nm and at 401 and 420 nm, respectively. The maximum absorption wavelength of poly(dihexylfluorene) in the solid state also coincides with the maximum emission wavelength of POSS-FL3 in the solid state.[16] The PL quantum efficiency of POSS-FL3 in the solid state was estimated to be 1.76 relative to that of poly(dihexylfluorene). The PL emission spectra and PL efficiencies of POSS-FL3 in THF solution and in the solid state indicate that POSS-FL3 is likely to be an efficient POSS-based blue light-emitting nanomaterial. In addition, the good spectral overlap of the POSS-FL3 emission wavelengths with the poly(dihexylfluorene) absorption wavelength indicates the potential usefulness of POSS-FL3 as a dopant for enhancing the quantum efficiencies of poly(dialkylfluorene)s through energy transfer.[15] We investigated the properties of EL devices fabricated from POSS-FL3 and poly(dihexylfluorene) blends in the discussion that follows. This is the first report of the energy transfer from a blue emissive nanosized material with a shorter emissive wavelength to a blue emissive material with a longer emissive wavelength.

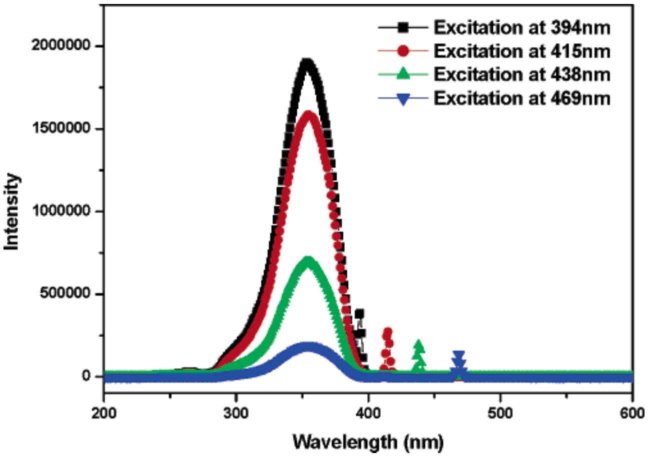


Figure 2. PL excitation spectra of POSS-FL3.

Figure 2 shows the PL excitation spectra of POSS-FL3 for various excitation wavelengths. Only one band with a maximum wavelength of 353−355 nm was observed for all of these excitation wavelengths. From these results, we conclude that the maximum (at 394 nm) and shoulder peaks (at 415, 438, and 469 nm) in the PL spectrum of POSS-FL3 in THF solution (Figure 1) are derived from the same excitation mode.

Figure 3a shows a SEM image of POSS-FL3. POSS-FL3 molecules aggregate with each other and form particles ∼10−20 nm in size, as shown in Figure 3a. The aggregation between POSS-FL3 molecules does not result in the significant aggregation of the terfluorenes appended on the POSS core because the nanosized POSS cores[19] interrupt the effective aggregation of the terfluorene moieties, as depicted in Figure 3b.[20]

Cyclic voltammetry (CV) was carried out to investigate the electrochemical properties of POSS-FL3, and the cyclic voltammogram is shown in Figure 4. A POSS-FL3 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.[6,16] The 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 POSS-FL3 in the cyclovoltammetric cell, the measurements were calibrated using ferrocene as the standard of oxidation. The HOMO energy level of POSS-FL3 was estimated to be 5.75 eV from the first oxidation process. The band gap energy of POSS-

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(18) Terfluorene-based oligomer and polymer derivatives: (a) Wong, K. T.; Chien, Y. Y.; Chen, R. T.; Wang, C. F.; Lin, Y. T.; Chiang, H. H.; Hsieh, P. Y.; Wu, C. C.; Chou, C. H.; Su, Y. O.; Lee, G. H.; Peng, S. M. *J. Am. Chem. Soc.* **2002**, *124*, 11576. (b) Zhang, Q.; Chen, J. S.; Cheng, Y. X.; Geng, Y. H.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. *Synth. Met.* **2005**, *152*, 229. (c) Beaupre, S.; Ranger, M.; Leclerc, M. *Macromol. Rapid Commun.* **2000**, *21*, 1013. (d) Wu, F. I.; Dodda, R.; Reddy, D. S.; Shu, C. F. *J. Mater. Chem.* **2002**, *12*, 2893. (e) Tsolakis, P. K.; Kallitsis, J. K. *Chem. Eur. J.* **2003**, *9*, 936. (f) Burnell, T.; Cella, J. A.; Donahue, P.; Duggal, A.; Early, T.; Heller, C. M.; Liu, J.; Shiang, J.; Simon, D.; Slowinska, K.; Sze, M.; Williams, E. *Macromolecules* **2005**, *38*, 10667.

(19) Laine et al. demonstrated that the diameter of the POSS core is about 0.5 nm and that the diameter of POSS-based materials containing organic chromophores is over 1.2 nm (ref 10).

(20) (a) Zhang, X.; Jenekhe, S. A.; Perlstein, J. *Chem. Mater.* **1996**, *8*, 1571. (b) Jenekhe, S. A.; Zhang, X.; Chen, X. L.; Choong, V.-E.; Gao, Y.; Hsieh, B. R. *Chem. Mater.* **1997**, *9*, 409. (c) Alam, M. M.; Tonzola, C. J.; Jenekhe, S. A. *Macromolecules* **2003**, *36*, 6577−6587.

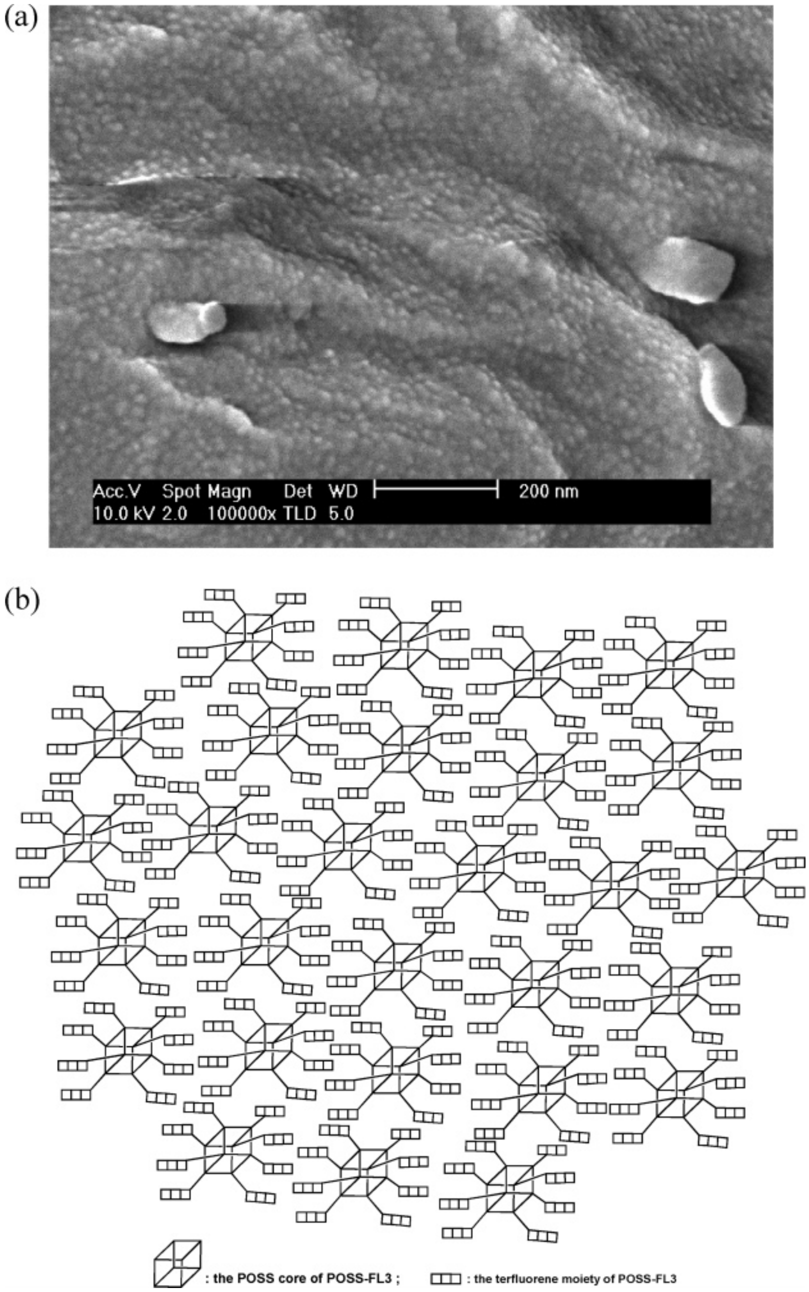

Figure 3. (a) SEM image of POSS-FL3. (b) The nanosized POSS cores of POSS-FL3 interrupt the aggregation of terfluorenes appended to the POSS cores.

FL3 was estimated from the absorption edge of the UV spectrum of POSS-FL3 in the solid state, and the LUMO energy level of POSS-FL3 was obtained from the difference between the HOMO energy level and the band gap energy.[6,16] The LUMO energy level and the band gap energy of POSS-FL3 were found to be 2.66 and 3.09 eV, respectively. The LUMO and HOMO energy levels of POSS-FL3 are elevated compared to those of polydihexylfluorene, and the band gap energy (3.09 eV) of POSS-FL3 is larger than that of polydihexylfluoene (2.91 eV).[16,18]

A single-layered EL device with the configuration ITO/PEDOT:PSS/POSS-FL3/Ca (500 nm)/Al (800 nm) was fabricated.[6] PEDOT:PSS was spin-coated on an ITO substrate with a film thickness of 40 nm and baked at 150 °C for 60 min. A POSS-FL3 film was coated onto the PEDOT:PSS layer with a film thickness of 30 nm from a chlorobenzene solution of POSS-FL3. The metals Ca and Al were consecutively deposited onto the POSS-FL3 layer. The EL spectrum of the POSS-FL3 device is shown in Figure 5a, and the maximum EL peaks of the device appear at 400, 422, and 464 nm. The emission is in the blue region with CIE coordinates of (0.22, 0.25). The additional peak at 464 nm in the EL spectra is not observed in PL spectra. It is not likely that the additional peak in EL spectra occur due to the formation of fluorenones by the oxidation of fluorene units in POSS-FL3 from the report of Jenekhe et al.,[21] but the origin of the peak remains unclear. The maximum brightness (260 cd/m^2 at 10 V) of the POSS-FL3 device was higher than that (170 cd/m^2 at 9 V) of the poly(dihexylfluorene) device. The external quantum efficiency (EQE) of the device was 0.0164% at 10 V, whereas that of the poly-

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(21) The emission of a terfluorene oligomer containing a fluorenone unit was observed at much longer wavelengths near 530 nm in: Kulkarni, A. P.; Kong, X.; Jenekhe, S. A. *J. Phys. Chem. B* **2004**, *108*, 8689.

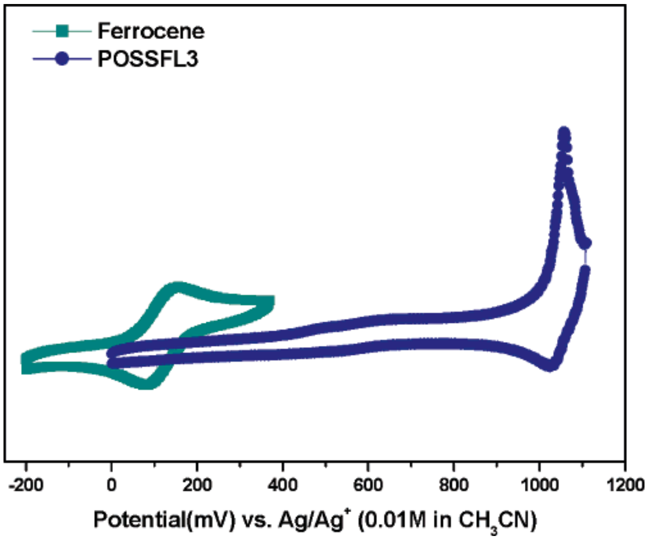

Figure 4. Cyclic voltammogram of POSS-FL3.

(dihexylfluorene) device was 0.0095% at 9 V. It seems that the higher EQE of the POSS-FL3 device is derived from the isolation of the terfluorenes by the nanosized POSS cores and the resulting suppression of aggregation of the terfluorenes appended to the POSS cores. Interestingly, the external quantum efficiencies in EL devices of POSS-FL3 doped poly(dihexylfluorene) blends are 4−8 times higher than that (0.0095%) of poly(dihexylfluorene), as shown in Figure 5c.[15] The external quantum efficiencies of the POSS-FL3/polydihexylfluorene blend system devices containing 5 and 25 wt % POSS-FL3 were found to be 0.0392% at 6 V and 0.0747% at 5 V, respectively.

Conclusion

We synthesized the POSS-based blue-light electroluminescent nanoparticle, POSS-FL3, which contains a terfluorene chromophore on each of its eight arms and exhibits good solution processing properties. The good spectral overlap of the maximum absorption wavelength (391 nm in THF solution) of poly(dihexylfluorene) with the maximum emission wavelengths (394 nm in THF solution) of POSS-FL3 suggests that POSS-FL3 can be used as a dopant of blue light-emissive conjugated polymers such as polyfluorenes to increase their quantum efficiencies through energy transfer and the isolation of the chromophores, as well as in the applications requiring electroluminescent nanoparticles. To the best of our knowledge, POSS-FL3 is the first electroluminescent POSS-based nanoparticle emitting visible (blue) light, and nanoparticle-cored dopant chromophore that can be used to enhance the quantum efficiency of a host blue light-emitting conjugated polymer through energy transfer. Surprisingly, the external quantum efficiencies in EL devices of POSS-FL3 doped poly(dihexylfluorene) blends were found to be 4−8 times higher than that of poly(dihexylfluorene). In future research, we plan to fabricate optimal EL devices containing POSS-FL3 or blends of POSS-FL3 with polyfluorenes.

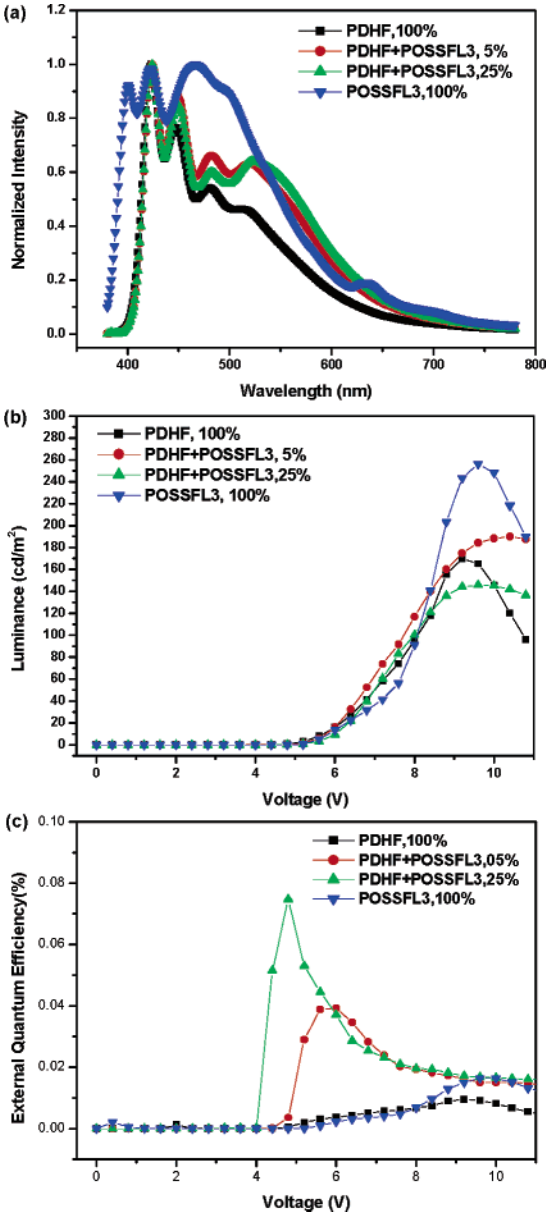

Figure 5. (a) EL spectra of the devices with ITO/PEDOT:PSS/emissive material/Ca/Al configurations. (b) Voltage−luminance (*V*−*L*) characteristics of the devices. (c) Voltage−external quantum efficiency characteristics of the devices.

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

Supporting Information Available: ^{1}H NMR of **8** and **10** (POSS-FL3); DSC thermogram and TGA traces of POSS-FL3 (**10**). This material is available free of charge via the Internet at http://pubs.acs.org.

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