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Poly(*p*-phenylene vinylene)s Wrapped with 1,3,5-Phenylene-Based Rigid Dendrons

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Novel poly(*p*-phenylene vinylene)s (PPVs) **6** and **7** wrapped with rigid 1,3,5-phenylene dendrons have been synthesized by using stepwise Suzuki coupling reactions and the following polymerization. The synthesized dendritic PPVs possess high thermal stability and good film-forming properties. The fluorescence spectra of the polymer films demonstrate the effectiveness of side chains in preventing π-stacking among conjugated backbones without causing undesirable shifts in fluorescence spectra. Electroluminescent devices have been constructed in the configuration ITO/PEDOT:PSS/**6** or **7**/Ca/Al, and their light-emitting and electrical characteristics have been investigated. The efficiency of organic light-emitting diodes (OLEDs) devices is strongly affected by the size of the phenylene dendron. The color of OLED devices could be tuned by the doping of fluorescence into the dendritic PPV layer.

Introduction

As a result of extended π-electron delocalization along a conjugated polymer backbone, conjugated organic polymers such as poly(*p*-phenylene vinylene)s (PPVs), poly(*p*-phenylene ethynylene)s (PPEs), and poly(*p*-phenylene)s (PPPs) have been extensively studied as organic semiconductive materials because of their desirable optical, electronic, and mechanical properties. These conjugated polymer materials are finding broad applicability in organic light-emitting diodes (OLEDs),[1] solar cells,[2−4] field-effect transistors,[5−7] and chemosensory devices.[8,9] Interchain interactions among conjugated polymers are an important determinant of the fluorescence and electronic properties.[10,11] The aggregation of conjugated polymers results in the low fluorescence quantum yields and peak shifting of the fluorescence spectra. To date, spatially isolated conjugated polymers have been synthesized to control interchain interactions. Swager et al. reported the enhancement of fluorescence quantum yields of PPVs and PPEs by the incorporation of rigid three-dimensional pentiptycene moieties and the potential for artificial fluorescence chemosensors to detect the vapor of explosives.[12−14] Müllen et al. synthesized nonaggregating polyfluorenes by using bulky pentaphenylene side chains as shielding and solubilizing groups.[15] Highly branched dendritic architectures have also been used to prevent the aggregation of conjugated polymers. Schlüter and Rabe synthesized cylindrical dendronized polymers by the attachment of semiflexible poly(benzyl ether) dendrons with rigid PPP backbones through the Suzuki coupling reaction.[16] Aida et al. reported the structural dependence of photoluminescence properties of PPEs wrapped with poly(benzyl ether) dendrons in solution.[17] Bao et al. prepared dendronized PPVs by Heck coupling of dendritic monomer with divinylbenzene.[18] Conjugated polymers surrounded by three-dimensional bulky groups or dendritic wedges can isolate the conjugated backbones from one another in solution and the solid state, thereby enhancing optical properties due to reduced self-quenching.

OLEDs have attracted interest because of their potential applications in flat panel displays and flat light sources.[19,20] Light-emitting layers within OLED devices have been

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formed by vacuum evaporation or solution processing. Solution processing such as spin-casting and ink-jet printing offers a low-cost approach to large-area full-color displays. In this context, solution-processible conjugated polymers and fluorescent/phosphorescent molecules have been developed for use as the light-emitting layer in OLEDs. A variety of fluorescent/phosphorescent dendrimers have been successfully used in the fabrication of OLEDs by means of a solution processing. Wrapping of a fluorescence/phosphorescence core with dendritic architectures inhibited both energy transfer among cores and self-quenching. Furthermore, dendritic architectures enable appropriate spatial arrangements for hole-transporting, electron-transporting, and light-emitting components within a single molecule. Thompson and Fréchet et al. reported fine color tunings of OLEDs by the control of electronic interactions between a fluorescence core and peripheral electroactive moieties within single light-emitting dendrimers.[21] Samuel et al. have developed dendrimers composed of a phosphorescent *fac*-tris(2-phenylpyridine)iridium complex core and rigid 1,3,5-polyphenylene dendrons for use as the light-emitting layer in OLEDs.[22−25] The attachment of rigid conjugated dendrons with a phosphorescent core can be tuned to control the hole mobility within the emissive layer and the degree of intermolecular interaction among cores. The precise control of chemical structures of dendrimers around fluorescence or phosphorescence molecules would enable significant improvements in the efficiency and stability of OLEDs. Previously, we also reported the syntheses of 1,3,5-phenylene-based dendrimers having functional cores and investigated the effects of rigid dendron units on the functionalities of cores.[26−29] While optical properties of conjugated polymers wrapped with semiflexible dendrons have been reported,[16] the effect of rigid dendrons on properties of conjugated polymers has not been as extensively explored. Here we report the synthesis of PPVs wrapped with rigid 1,3,5-polyphenylene dendrons and the fabrication of OLEDs that contain a solution processed light-emitting layer of dendronized PPVs.

Experimental Section

General Methods. All starting materials were obtained from commercial suppliers and used as received. All moisture-sensitive reactions were performed under an atmosphere of nitrogen. Solvents, such as toluene, tetrahydrofuran (THF), and CH_2Cl_2, were freshly distilled. Column chromatography was carried out on Wakogel C-200. Analytical TLC was performed with commercial Merck plates coated with silica gel 60 F_{254}. Recycling preparative gel permeation chromatography was carried out by a JAI recycling preparative HPLC using $CHCl_3$ as an eluent. All NMR spectra were recorded on a Bruker AVANCE 400 FT-NMR spectrometer operating at 399.65 MHz for ^1H NMR and 100.61 MHz for ^{13}C NMR. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS), and carbon chemical shifts are reported in parts per million downfield of TMS using the resonance of the deuterated solvent as an internal standard. Matrix-assisted laser desorption/ionization (MALDI) mass spectra were obtained using dithranol as the matrix on a PerSeptive Biosystem Voyager-DE PRO spectrometer. IR spectra were measured on a JASCO FS-420 spectrometer. UV−vis and fluorescence spectra were recorded on a JASCO V-570 and a JASCO FP-750. GPC measurements were carried out using a Showa Denko GPC KF-804L column (8.0 × 300 mm) and THF as eluent and a flow rate of 1.0 mL min^{-1}. The boronic acid terminated 1,3,5-phenylene dendrons **1** and **2** were prepared by a literature method.[30]

Monomer Synthesis. ***3-COOCH$_3$.*** 2-Bromoterephthalic acid dimethylester (0.43 g, 1.59×10^{-3} mol) and the first-generation 1,3,5-phenylene dendron **1** (0.4 g, 1.32×10^{-3}mol) were dissolved in the mixed solvent of toluene (4 mL), THF (10 mL), and 2.0 mol L^{-1} Na_2CO_3 aqueous solution (10 mL). After degassing by nitrogen gas, $Pd(PPh_3)_4$ (0.05 g, 3.96×10^{-5} mol) was added to the mixed solution. The reaction mixture was refluxed for 48 h under a nitrogen atmosphere. After 48 h, the reaction mixture was diluted with diethyl ether (50 mL) and washed with water (3 × 50 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel by eluting with CH_2Cl_2/petronium ether (1:1) and recycling preparative GPC. Yield: 59%. $R_f = 0.40$ (CH_2Cl_2/petronium ether (1:1, v/v)). FT-IR (KBr): $\nu = 1725$ cm^{-1} (−$COOCH_3$). ^1H NMR ($CDCl_3$): $\delta = 8.16$ (s, 1H, Ph), 8.10 (d, $J = 7.8$ Hz, 1H, Ph), 7.88 (d, $J = 8.1$ Hz, 1H, Ph), 7.80 (s, 1H, Ph), 7.57 (d, $J = 7.8$ Hz, 4H, Ph), 7.50 (s, 2H, Ph), 7.28 (d, $J = 8.1$ Hz, 4H, Ph), 3.95 (s, 3H, −COOCH_3), 3.66 (s, 3H, −COOCH_3), 2.41 (s, 6H, −CH_3). Anal. Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 79.8; H, 5.9.

The synthetic procedures for **4-COOCH$_3$** and **5-COOCH$_3$** are similar to that for **3**.

4-COOCH$_3$. This was prepared from 2-bromoterephthalic acid dimethylester and the second-generation 1,3,5-phenylene dendron **2**. The crude product was purified by column chromatography on silica gel by eluting with CH_2Cl_2/petronium ether (1:1, v/v) and recycling preparative GPC. Yield: 42%. $R_f = 0.20$ (CH_2Cl_2/petronium ether (1:1, v/v)). FT-IR (KBr): $\nu = 1727$ cm^{-1} (−$COOCH_3$). ^1H NMR ($CDCl_3$): $\delta = 8.21$ (s, 1H, Ph), 8.12 (d, $J = 7.8$ Hz, 1H, Ph), 8.00 (s, 1H, Ph), 7.92 (d, $J = 8.1$ Hz, 1H, Ph), 7.83 (s, 4H, Ph), 7.79 (s, 2H, Ph), 7.66 (s, 2H, Ph), 7.60 (d, $J = 7.8$ Hz, 8H, Ph), 7.28 (d, $J = 8.1$ Hz, 8H, Ph), 3.94 (s, 3H, −COOCH_3), 3.70 (s, 3H, −COOCH_3), 2.41 (s, 12H, −CH_3). ^{13}C NMR ($CDCl_3$): 168.4, 166.1, 142.4, 142.2, 142.0, 141.8, 141.4, 138.2, 137.4, 135.0, 132.6, 131.8, 129.9, 129.6, 128.5, 127.2, 126.6, 125.8, 125.2, 124.9, 52.4, 21.1. MALDI-TOF-Ms: $m/z = 783$ ($[M + H]^+$, 100%).

5-COOCH$_3$. This was prepared from 2,5-dibromoterephthalic acid dimethylester and the first-generation 1,3,5-phenylene dendron **1**. The crude product was purified by column chromatography on silica gel by eluting with CH_2Cl_2/petronium ether (1:1, v/v) and recycling preparative GPC. Yield: 29%. $R_f = 0.45$ (CH_2Cl_2/

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petronium ether (1:1, v/v)). FT-IR (KBr): $\nu = 1718$ cm^{-1} ($-COOCH_3$). ^{1}H NMR ($CDCl_3$): $\delta = 7.96$ (s, 2H, Ph), 7.81 (s, 2H, Ph), 7.60 (s, 4H, Ph), 7.56 (d, $J = 8.1$ Hz, 8H, Ph), 7.28 (d, $J = 7.8$ Hz, 8H, Ph), 3.68 (s, 6H, $-COOCH_3$), 2.41 (s, 12H, $-CH_3$). ^{13}C NMR ($CDCl_3$): $\delta = 168.6$, 141.6, 141.2, 140.7, 137.9, 137.4, 133.4, 132.1, 129.6, 127.1, 125.7, 125.0, 52.4, 21.1. MALDI-TOF-Ms: $m/z = 706$ ($[M + H]^+$, 100%).

3-CH$_2$OH. A solution of **3** (0.35 g, 7.77×10^{-4}mol) in 5 mL of dry THF was added dropwise into a solution of $LiAlH_4$ (0.10 g, 2.63×10^{-3}mol). The reaction mixture was stirred for 2 h at room temperature. After 2 h, an aqueous solution of NaOH (15% w/w, 1 mL) was added carefully to the reaction mixture to destroy the excess of $LiAlH_4$. The mixture was filtered, and the filtrate was evaporated to dryness. The product was used for further reaction without purification. Yield: 95%. FT-IR (KBr): disappearance of peak at 1725 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.80$ (s, 1H, Ph), 7.54$-$7.60 (m, 7H, Ph), 7.42 (d, $J = 7.8$ Hz, 1H, Ph), 7.39 (s, 1H, Ph), 7.26 (d, $J = 8.1$ Hz, 4H, Ph), 4.73 (s, 2H, $-CH_2OH$), 4.71 (s, 2H, $-CH_2OH$), 2.41 (s, 6H, $-CH_3$).

The synthetic procedures for **4-CH$_2$OH** and **5-CH$_2$OH** are similar to that for **3-CH$_2$OH**.

4-CH$_2$OH. This was prepared from **4**. Yield: 94%. FT-IR (KBr): disappearance of peak at 1727 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 8.02$ (s, 1H, Ph), 7.86 (s, 4H, Ph), 7.79 (s, 4H, Ph), 7.61 (m, 9H, Ph), 7.46 (m, 2H, Ph), 7.27 (d, $J = 8.1$ Hz, 8H), 4.74 (s, 2H, $-CH_2OH$), 4.71 (s, 2H, $-CH_2OH$), 2.32 (s, 12H, $-CH_3$).

5-CH$_2$OH. This was prepared from **5**. Yield: 96%. FT-IR (KBr): disappearance of peak at 1718 cm^{-1}). ^{1}H NMR ($CDCl_3$): $\delta = 7.84$ (s, 2H, Ph), 7.68 (s, 4H, Ph), 7.60$-$7.63 (m, 10H, Ph), 7.28 (d, $J = 7.8$ Hz, 8H, Ph), 4.73 (s, 4H, $-CH_2OH$), 2.41 (s, 6H, $-CH_3$).

3-CH$_2$Cl. 3-CH_2OH (0.78 g, 1.98×10^{-3}mol) was dissolved in 5 mL of dry CH_2Cl_2 and 0.1 mL of dry dimethylformamide (DMF). $SOCl_2$ (0.32 mL, 4.35×10^{-3}mol) was added to this solution, and the reaction mixture was stirred for 1 h. The solvent and excess $SOCl_2$ were removed under vacuum. The resulting solid was dissolved in Et_2O and then washed with water, dried over $MgSO_4$, and evaporated. The product was purified by column chromatography on silica gel by eluting with CH_2Cl_2/petronium ether (1:1 v/v) and recycling preparative GPC. Yield: 65%. $R_f = 0.70$ (CH_2Cl_2/petronium ether (1:1 v/v)). ^{1}H NMR ($CDCl_3$): $\delta = 7.82$ (s, 1H, Ph), 7.57$-$7.60 (m, 7H, Ph), 7.51 (d, $J = 7.8$ Hz, 1H, Ph), 7.41 (s, 1H, Ph), 7.27 (d, $J = 7.84$ Hz, 4H, Ph), 4.62 (s, 2H, $-CH_2Cl$), 4.61 (s, 2H, $-CH_2Cl$), 2.40 (s, 6H, $-CH_3$). ^{13}C NMR ($CDCl_3$): $\delta = 142.5$, 141.8, 140.5, 137.9, 137.5, 135.3, 131.1, 130.4, 129.6, 128.2, 127.2, 126.4, 125.0, 45.6, 44.1, 21.1. Anal. Calcd for $C_{28}H_{24}Cl_2$: C, 77.96; H, 5.61. Found: C, 77.8; H, 5.7.

The synthetic procedures for **4-CH$_2$Cl** and **5-CH$_2$Cl** are similar to that for **3-CH$_2$Cl**.

4-CH$_2$Cl. This was prepared from **4-CH$_2$OH**. The crude product was purified by column chromatography on silica gel by eluting with CH_2Cl_2/petronium ether (1:1 v/v) and recycling preparative GPC. Yield: 78%. $R_f = 0.75$ (CH_2Cl_2/petronium ether (1:1, v/v)). ^{1}H NMR ($CDCl_3$): $\delta = 8.02$ (s, 1H, Ph), 7.86 (s, 4H, Ph), 7.79 (d, $J = 7.3$ Hz, 1H, Ph), 7.61 (d, $J = 8.1$ Hz, 8H, Ph), 7.47 (s, 1H, Ph), 7.27 (d, $J = 7.8$ Hz, 8H, Ph), 4.65 (s, 2H, $-CH_2Cl$), 4.63 (s, 2H, $-CH_2Cl$), 2.41 (s, 12H, $-CH_3$). ^{13}C NMR ($CDCl_3$): 142.5, 142.3, 142.2, 141.7, 140.7, 138.2, 138.0, 137.4, 135.3, 131.3, 130.5, 129.6, 128.3, 127.2, 125.7, 125.2, 124.9, 121.8, 45.6, 44.2, 21.1. MALDI-TOF-Ms: $m/z = 763$ ($[M + H]^+$, 100%).

5-CH$_2$Cl. This was prepared from **5-CH$_2$OH**. The crude product was purified by column chromatography on silica gel by eluting with CH_2Cl_2/petronium ether (1:1, v/v) and recycling preparative GPC. Yield: 84%. $R_f = 0.70$ (CH_2Cl_2/petronium ether (1:1, v/v)). ^{1}H NMR ($CDCl_3$): $\delta = 7.84$ (s, 2H, Ph), 7.67 (s, 4H, Ph), 7.61 (m, 10H, Ph), 7.28 (d, $J = 8.3$ Hz, 8H, Ph), 4.65 (s, 4H, $-CH_2Cl$), 2.41 (s, 12H, $-CH_3$). ^{13}C NMR ($CDCl_3$): $\delta = 141.9$, 141.8, 140.2, 137.9, 137.5, 135.5, 132.6, 129.6, 127.2, 126.4, 125.1, 44.0, 21.1. MALDI-TOF-Ms: $m/z = 688$ ($[M + H]^+$, 100%).

Polymer Synthesis. *First Generation Dendronized PPV **6**.* Potassium *t*-butoxide (0.16 g, 1.39×10^{-3}mol) and 18-crown-6-ether (0.01 g) were dissolved in 5.0 mL of dry toluene. Under an atmosphere of nitrogen, a toluene solution of **3-CH$_2$Cl** (0.1 g, 2.32×10^{-4}mol) was added to this solution. This was left to stir for 24 h at room temperature and refluxed for 24 h. The reaction mixture was then precipitated into methanol, and the raw product was reprecipitated from THF in acetone three times. The resulted precipitate was collected, washed with acetone, and dried in vacuo. Yield: 40 mg (44%). ^{1}H NMR ($CDCl_3$): $\delta = 7.5-7.8$ (br, Ph), 7.2$-$7.5 (br, Ph), 6.9$-$7.2 (br, Ph), 6.1$-$6.4 (br, $-CH{=}CH-$), 2.40 (br, $-CH_3$). UV$-$vis ($CHCl_3$): $\lambda_{max} = 257$ and 429 nm. $M_{GPC} = 39$ KDa, PDI = 2.5.

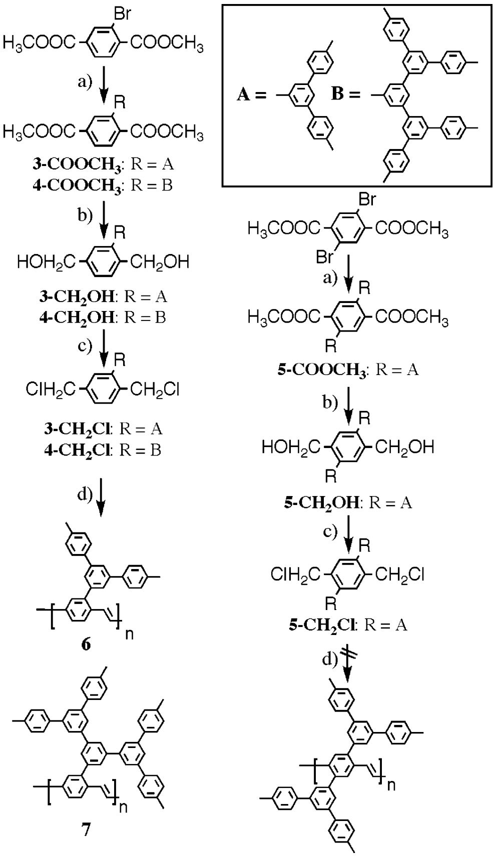
*Second Generation Dendronized PPV **7**.* Yield: 55%. ^{1}H NMR ($CDCl_3$): $\delta = 7.5-7.8$ (br, Ph), 7.2$-$7.5 (br, Ph), 6.9$-$7.2 (br, Ph), 6.1$-$6.4 (br, $-CH{=}CH-$), 2.40 (br, $-CH_3$). UV$-$vis ($CHCl_3$): $\lambda_{max} = 260$ and 418 nm. $M_{GPC} = 160$ KDa, PDI = 3.2.

Device Fabrication. To fabricate the OLEDs, 50 nm thick poly(3,4-ethylenendioxythiophene)/polystyrene sulfonic acid (PEDOT:PSS) films were first deposited on pre-cleaned indium tin oxide (ITO)-coated glass substrate by spin-coating and then cured at 120 °C in air for 30 min. The film of the emitting layer was spin-coated with a toluene solution of **6** or **7** (concentration: 10 mg/mL) at a spin rate of 1200 rpm for 1 min. The dried spin-coated films were then transferred to the chamber of a vacuum evaporator. The Ca/Al (6 nm/ 200 nm) cathode was evaporated with a base pressure less than 10^{-6} Torr. The emissive area of the device was 2 mm × 2 mm. All the experiments were carried out at room temperature under ambient conditions.

Results and Discussion

First- and second-generation dendronized PPVs **6** and **7** were synthesized as depicted in Scheme 1. The first- and second-generation phenylene dendrons were synthesized by using the convergent method developed by Miller et al. with *p*-tolylboronic acid and 3,5-dibromo-1-(trimethylsilyl)-benzene as starting materials.[30] Suzuki coupling reactions between dendrons having a boronic acid and 2-bromoterephthalic acid dimethylester led to the formation of **3-COOCH$_3$** and **4-COOCH$_3$** in 59 and 42% yields, respectively. The reduction by $LiAlH_4$ and chlorination with $SOCl_2$ of **3-COOCH$_3$** and **4-COOCH$_3$** gave the corresponding monomers **3-CH$_2$Cl** and **4-CH$_2$Cl**. The other monomer **5-CH$_2$Cl** possessing two dendron units was synthesized from 2,4-dibromoterephthalic acid dimethylester. All compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy, Fourier tranform infrared (FT-IR), and elemental analysis. The synthesized monomers **3-CH$_2$Cl** and **4-CH$_2$Cl** were polymerized by reaction with excess KO^{t}Bu in toluene to give dendronized PPVs **6** and **7**. Gel permeation chromatography (GPC) analyses (THF as the eluent) of **6** and **7** revealed a monomodal distribution with weight-average molecular weights (M_w) of 3.9×10^4 g/mol (PDI = 3.8) and 1.6×10^5 g/mol (PDI = 3.6) relative to polystyrene standards. The resulting polymers **6** and **7** exhibit good solubility in toluene, THF, and chlorinated organic solvents

Scheme 1. Syntheses of the Precursors and Dendritic PPVs 6 and 7[a]



[a] (a) A−B(OH)$_2$ or B−B(OH)$_2$, Pd(PPh$_3$)$_4$, toluene, THF, Na$_2$CO$_3$(aq), reflux for 48 h; **3-COOCH$_3$**, 59%; **4-COOCH$_3$**, 42%; **5-COOCH$_3$**, 29%. (b) LiAlH$_4$, THF, rt for 2 h, 95%. (c) SOCl$_2$, CH$_2$Cl$_2$, DMF; **3-CH$_2$Cl**, 65%; **4-CH$_2$Cl**, 78%; **5-CH$_2$Cl**, 84%. (d) *t*-BuOK, 18-crown-6-ether, toluene, reflux for 24 h.

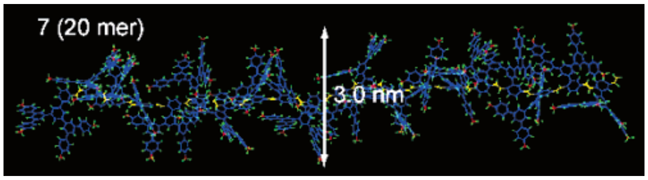


Figure 1. Energy-minimized structure of **7** (20 mer).

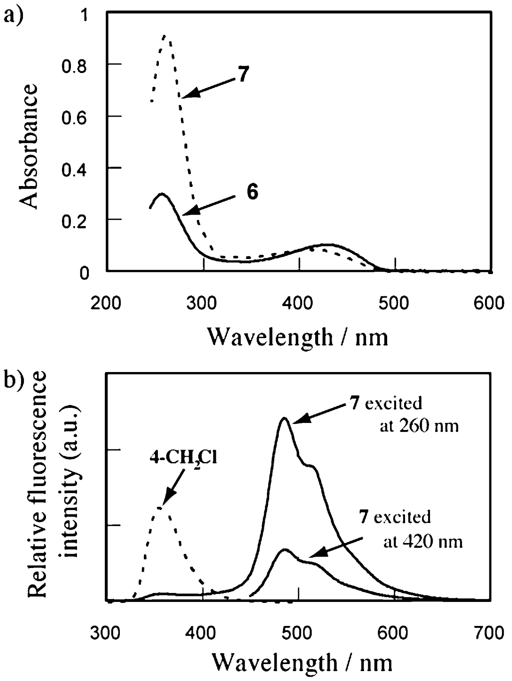


Figure 2. (a) Absorption spectra of polymers **6** and **7** in CH$_2$Cl$_2$. (b) Fluorescence spectra of **4-CH$_2$Cl** upon excitation at 260 nm and **7** upon excitation at 260 and 420 nm in degassed CH$_2$Cl$_2$ at room temperature.

(above 30 mg/mL) without any flexible side chains, and they exhibit an excellent film-forming property by spin-coating from the solution. The high solubility indicates the effective suppression of interchain interaction among conjugated PPV backbones caused by the wrapping with rigid phenylene dendron units. The products exhibited an IR absorption band around 935 cm^{-1} arising from the C−H out-of-plane bending of *trans*-vinylene.[31] Differential scanning calorimetry (DSC) of **7** exhibits only a phase transition at 200 °C. Temperature-controlled polarizing microscopy did not demonstrate a birefringent texture for a thermotropic liquid crystalline phase. Thus, we attributed the transition point observed in DSC analysis to a glass transition (T_g). To synthesize soluble PPVs, solubilizing groups such as branched alkyl and alkoxy groups have been attached to the conjugated backbone. The introduction of these flexible solubilizing groups reduced T_g, causing the resultant thermal instability of OLED devices.[32,33] The dendronized PPVs **6** and **7** having rigid phenylene dendrons exhibited excellent thermal stability while maintaining their solubility. According to the computer-generated modeling of **7**, as shown in Figure 1, the synthesized dendronized PPV **7** wrapped with the second-generation dendron wedges exhibited a cylindrical shape, and the conjugated PPV backbone was encapsulated in the cylindrical rigid dendritic shell with a thickness of approximately 1.5 nm. In contrast, the polymerization of the much bulkier monomer **5-CH$_2$Cl** having two first generation dendrons gave only oligomers with up to five repeat units in low yield. It was concluded that the polymerization of dendritic monomers **3-CH$_2$Cl** and **4-CH$_2$Cl** gave the desired high-molecular-weight PPVs **6** and **7** wrapped in the rigid phenylene dendrons.

The absorption spectra of the dendronized PPVs **6** and **7** along with dendritic monomers **3-CH$_2$Cl** and **4-CH$_2$Cl** were measured in CH$_2$Cl$_2$. The dendronized PPVs **6** and **7** displayed a broad absorption band in the visible region around 420 nm. An appearance of this new board absorption band indicates an extended π-electronic conjugation along the backbones caused by the polymerization of **3-CH$_2$Cl** and **4-CH$_2$Cl** (Figure 2a).[34−36] The dendronized PPV **7** decorated with the second-generation phenylene dendrons showed a 10 nm blue-shift of the maximum with respect to that of **6**. This blue-shift is due to reduction of interchain interactions

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or a sterically driven increase in the twist angle within the PPV backbone. An intense absorption band that was observed at 260 nm was ascribed to 1,3,5-phenylene dendron units. As the dendrimer generation increased, the absorption intensity corresponding to the dendron units in **7** is almost three times of that of the first generation **6**.

Steady-state fluorescence spectra of **7** and **4-CH$_2$Cl** in degassed CH$_2$Cl$_2$ are shown in Figure 2b. The dendronized PPVs **6** and **7** emitted a sharp fluorescence at 486 nm by the excitation of the conjugated backbone at 420 nm in CH$_2$Cl$_2$ (abs$_{420}$ nm $= 0.01$). The fluorescence intensity increased linearly as the polymer concentration increased up to abs$_{420}$ nm $= 0.1$. On the other hand, the lower-generation dendronized PPV **6** exhibited a red-shift and broadening of the fluorescence peak with increasing polymer concentration. From these results, the wrapping of conjugated PPV backbone with second-generation phenylene dendron units prevents the loss of photoexcited energy from the interchain aggregation in the ground state. The **4-CH$_2$Cl** monomer emitted strong fluorescence at 360 nm upon excitation of the dendron units. The emission from dendron units at 360 nm was overlapped with the absorption band of the PPV backbone. Recently, energy transfer interactions among chromophores within dendritic structures have been widely investigated to mimic some of the primary events of photosynthesis.[37−39] Upon excitation of the dendron units at 260 nm in CH$_2$Cl$_2$, **7** emitted a strong fluorescence at 486 nm and the fluorescence from the dendron units at 360 nm was very weak. Furthermore, the fluorescence intensity was higher than that observed upon excitation of the conjugated backbone at 420 nm as shown in Figure 2. This result indicated an efficient intramolecular singlet energy transfer from the phenylene dendron units to the focal PPV backbone. The efficiency of energy transfer was nearly 100% as estimated by the comparison between the excitation spectrum and the absorption spectrum.[40] The photons absorbed by the phenylene dendron units were transduced to the fluorescent emission from the conjugated PPV backbone through a highly efficient energy transfer. Dendrimer films with film thicknesses ranging between 50 and 90 nm were spun onto quartz substrate using toluene as the solvent. The spin-coated dendrimers films appeared to be uniform without any observable morphological features over the area of the substrate observed under an optical microscope. The fluorescence spectrum of a spin-coated film of **7** is almost the same as that of the dissolved polymer and does not exhibit any sign of aggregate formation (Figure 3). By contrast, films of the lower-generation polymer **6** exhibited a 24 nm red-shift with respect to the solution of **6**, and the emission spectrum was broadened with a long featureless tail extending into the red. Thermal treatment of poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene) (MEHPPV) at 160 °C for 30 min causes a significant red-shift and a reduction in fluorescence intensity in emission spectra due to heat-induced spatial re-organization of polymer packing. The emission spectra from the film of dendronized PPV **7** remained unaltered after thermal treatment. It appears that the prevention of direct contact of conjugated backbones contributes to the thermal stability of polymer films of **7**.

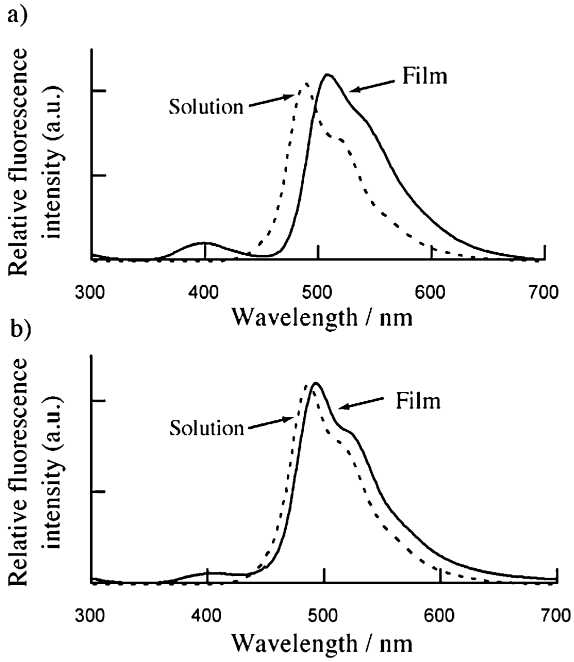

Figure 3. Fluorescence spectra of **6** (a) and **7** (b) upon excitation at 260 nm in thin films.

The current−voltage ($I-V$) and light output−voltage ($L-V$) characteristics of OLED devices fabricated with dendronized PPVs **6** and **7** as the emitting layer, ITO/PEDOT:PSS for the anode and calcium/aluminum for the cathode, are depicted in Figure 4.[41−46] Cleaned and oxygen-plasma-treated ITO substrates were coated with a layer of PEDOT:PSS which is known to facilitate hole injection and provide for planarization of the substrate. Light-emitting layers were formed by spin-coating from a toluene solution of **6** or **7** onto the ITO/PEDOT:PSS surface. Furthermore, a low-work-function cathode electrode was vacuum deposited. The average thicknesses of the emissive polymer films and of the PEDOT:PSS layer were 65 and 50 nm, respectively, and the active area of the OLED devices was 2 × 2 mm. The current density increased exponentially with the increasing forward bias voltage, which is a typical diode characteristic. Despite the same configuration ITO/PEDOT:PSS/**6** or **7**/Ca/Al, the brightness at the same voltage is much lower in **7** compared to that of **6**. The turn-on voltage, which was defined as the bias at a brightness of 1.0 cd/m^2, increases

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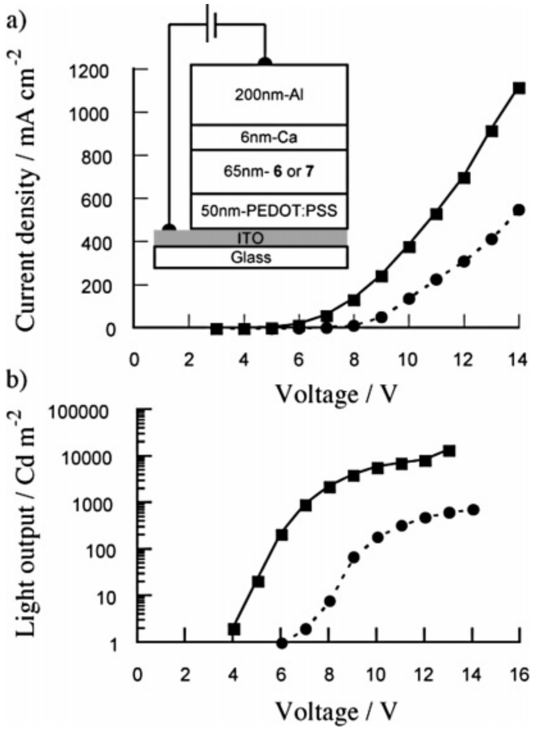

Figure 4. Current−voltage (a) and light output−voltage characteristics for ITO/PEDOT:PSS/**6** or **7**/Ca/Al devices. The inset shows the cross section of the EL devices.

from 3.8 V for **6** to 6.0 V for **7**, and the brightnesses for **6** and **7** at a driving voltage of 10.0 V were 9500 cd/m^2 and 400 cd/m^2, respectively. The luminescence efficiencies were 1.6 cd/A and 0.15 cd/A for **6** and **7**, respectively, at a driving voltage of 10.0 V. We also fabricated the OLED device by using MEHPPV ($M_w = 1.2 \times 10^5$ g/mol) as a light-emitting layer. The turn-on voltage and brightness at a driving voltage of 10 V for MEHPPV are 2.1 V and 15 000 cd/m^2. The luminescence efficiency decreases in the order **7** < **6** < MEHPPV, indicating that the attachment of higher generation dendrons causes a significant reduction in charge mobility. To understand the low efficiency in **7**, we estimated its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies. The work functions of MEHPPV and **7** were 5.3 and 5.7 eV as measured by photoelectron spectroscopy in air. The injection barrier for the hole in **7** is 0.7 eV referred to PEDOT:PSS (5.0 eV),[47,48] which is much larger than that in MEHPPV. Furthermore, the energy level of LUMO was deduced from the onset of the UV−vis spectrum and the work function (HOMO level). The estimated LUMO level of **7** (3.2 eV) is close to that of MEHPPV (3.1 eV), indicating that **7** and MEHPPV have the similar injection barriers for the electron referred to as the Ca/Al cathode. This large injection barrier for the injection of holes from the PEDOT:PSS layer beneath may lead to high operation voltage and low device efficiency.

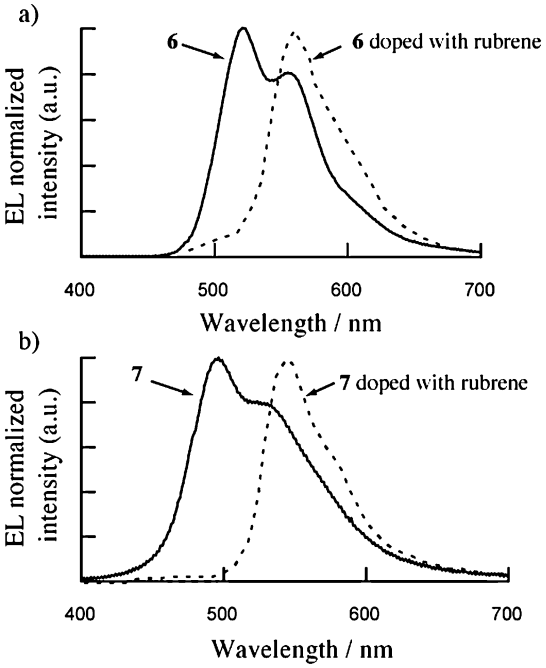

Figure 5. Normalized EL spectra from EL devices containing **6** (a) and **7** (b) and 10 wt % rubrene-doped **6** (a) and **7** (b). The device structure is ITO/PEDOT:PSS (50 nm)/polymer or polymer:dopant (65 nm)/Ca (6 nm)/Al.

The electroluminescence (EL) spectra of the three OLED devices using **6**, **7**, and MEHPPV as the light-emitting layer are shown in Figure 5. The EL spectra of **6** and MEHPPV reveal red shift as compared with those in solution, suggesting the formation of aggregation or excimers due to the interchain interaction among conjugated backbones. On the other hand, the EL spectrum of **7** closely matches the fluorescence spectra in solution and in spin-coated film with an emission maximum at 496 nm, indicating the suppression of excimer/aggregate formation during device operation. The emission color of OLED devices can be tuned by the doping with a fluorescent dye of a different color into the light-emitting layer.[49,50] The dopant is excited by the energy transfer from the host materials or the direct recombination at the dopant site resulting from carrier trapping in the operation of OLEDs. We investigated the color tuning of OLEDs by the doping of fluorescent dopant in the synthesized dendritic PPV host. The OLED devices were also fabricated by spin-coating from the mixed solution of 5,6,11,12-tetraphenylnaphthacene (rubrene) with **6**, **7**, or MEHPPV at 10 wt % of rubrene concentration. Rubrene, which has an emission peak at 565 nm, is used as a dopant. The overlap between emission from dendritic PPVs and absorption of rubrene (λ_{max} = 528 and 493 nm) enables highly efficient energy transfer from dendritic PPVs to rubrene. The spin-coated film of the mixture of rubrene and **7** was homogeneous and showed no irregular aggregates of rubrene as observed by optical microscopy and atomic force microscopy measurements. EL spectra of devices with rubrene doping of dendritic PPVs **6** and **7** are shown in Figure 5. When rubrene was admixed as a dopant in the layer of MEHPPV, light emission was not observed with the increasing applied voltage until 10.0 V, indicating a self-quenching caused by the formation of aggregates of rubrene in the MEHPPV host. On the other

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hand, the devices containing rubrene-doped dendritic PPV layers emitted yellow light from rubrene. Although the weak emission band at about 500 nm from **6** was observed in the device having the light-emitting layer of **6** doped with rubrene, the device of **7** doped with rubrene provided a pure rubrene emission peak. This suggests that the efficiency of energy transfer from the excitation of **7** to the rubrene molecule is higher than that in **6**. The dendritic PPV **7** has an internal space among the bulky second-generation phenylene dendron units as shown in Scheme 1. The dopant molecules can be included within the internal space in **7**. The inclusion of rubrene within the internal space produces a high-quality emitting layer, and the included rubrene molecules are excited by the energy transfer from the host or by direct excitation caused by carrier recombination at the dopant sites in the operation of OLEDs.

In conclusion, we have demonstrated a novel approach to nonaggregating PPVs using rigid 1,3,5-phenylene dendrons as shielding and solubilizing groups for designing promising solution-processable conjugated polymers for OLED applications. Dendritic PPVs having phenylene dendron side groups were synthesized by the Pd(0)-catalyzed Suzuki aryl–aryl coupling reaction and the polymerization. The synthesized dendritic PPVs possess high thermal stability and good film-forming properties. The fluorescence spectra of the polymer films demonstrate the effectiveness of side chains in preventing π-stacking among conjugated backbones without causing an undesirable shift in fluorescence spectra. Electroluminescent devices have been constructed using the dendritic PPVs **6** and **7**, and their light-emitting and electrical characteristics have been investigated. The efficiency of OLED devices is strongly affected by the size of the phenylene dendron. We have also demonstrated the tuning color of OLED devices by the doping of rubrene into the dendritic PPV layer.

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