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A Novel Triphenylamine-Substituted Poly(*p*-phenylenevinylene): Improved Photo- and Electroluminescent Properties

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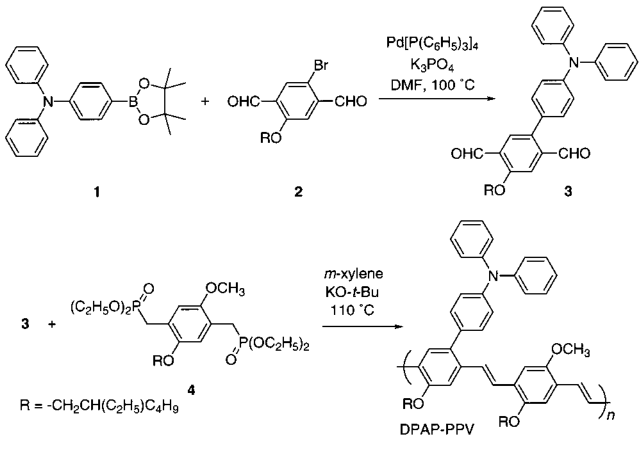
Poly(1,4-phenylenevinylene) (PPV) derivatives have attracted a great deal of attention because of their potential application as electroluminescence (EL) materials for light-emitting diodes (LEDs).[1,2] It is important, for achievement of high efficiency and luminance in an LED device, to prevent a self-quenching process due to formations of excimers in a solid state. Recently, various bulky substituents such as alkoxy, alkylsilyl, phenyl, and fluorenyl groups have been substituted at the 2- or 2,5-positions of the PPV backbone to suppress the intermolecular interactions that lead to the formation of excimers.[3−6] These PPV derivatives showed not only, of course, good solubility in common solvents but also high photoluminescence (PL) efficiency even in a solid state and high LED performance. On the other hand, a balanced injection of the electrons from a cathode and the holes from an anode is also essential for a high efficient LED. With respect to a promotion of electron transport, oxiadiazole derivatives have been introduced to PPVs as a side chain or into the PPV main chain because of their high electron affinity.[7−10] To enhance the hole-transport efficiency, there have been recent papers on PPV derivatives involving hole-transporting units such as a triphenylamine or carbazole group in the PPV main chain.[10−14] But to the best of our knowledge, there has been no report of PPV derivatives substituted with a hole-transporting side chain (except the paper on the synthesis of poly[2-(*N*,*N*-dimethylamino)-1,4-phenylenevinylene]).[15] Triphenylamine is characterized by a high hole-transporting ability and a bulky volume, which is appropriate for a side-chain substituent of the PPV backbone to realize both high fluorescence efficiency in the solid state and high hole mobility. We report here, for the first time, the synthesis of a fully conjugated PPV derivative substituted with triphenylamine, poly[5-(4′-(*N*,*N*-diphenylamino)-phenyl)-2-(2′-ethylhexyloxy)-1,4-phenylenevinylene-*alt*-5-methoxy-2-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (DPAP−PPV), and its highly emissive EL property over 29 000 cd/m^2 under a low driving voltage (≈8 V).

Scheme 1



The DPAP−PPV polymer was synthesized as shown in Scheme 1. We applied a Wittig−Horner reaction for the polymerization, that is, polycondensation between a terephthalaldehyde and xylene-bis(diethylphosphonate) derivative.[16] The key step was the synthesis of the terephthalaldehyde **3**[17] by a Suzuki coupling reaction between the pinacol borate **1**[18] and 2-alkoxy-5-bromoterephthalaldehyde **2**.[19] The polycondensation of **3** and **4**[19] was carried out in a *m*-xylene solution in the presence of potassium *tert*-butoxide at 100 °C.[20] The polymer was obtained as a bright orange powder, which was soluble in common solvents such as dichloromethane,

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(16) Triphenylamine-substituted monomer compounds suitable for a Gilch polymerization cannot be obtained by benzylhalogenation of xylene derivatives because the 4,4′-positions of triphenylamine reacted with electrophilic agents.

(17) To a DMF (47 mL) solution of **1** (3.50 g, 9.43 mmol), **2** (2.69 g, 7.86 mmol), and K_3PO_4 (2.50 g, 11.8 mmol) was added $Pd[P(Ph)_3]_4$ (181 mg, 0.157 mmol) at 60 °C under nitrogen. The mixture was stirred at 100 °C for 15 h and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated. The crude product was purified using a silica gel column with a hexane/dichloromethane (5/1) eluent. Recrystallization from hexane gave compound **3** (3.03 g, 76%) as an orange solid: ^{1}H NMR ($CDCl_3$, 500 MHz; ppm): δ 10.59 (s, 1H), 10.07 (s, 1H), 7.93 (s, 1H), 7.58 (s, 1H), 7.31−7.05 (m, 14H), 4.09 (dd, J = 5.5, 1.8 Hz, 2H), 1.84 (m, 1H), 1.58−1.34 (m, 8H), 0.99−0.88(m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz; ppm): δ 192.1, 189.4, 160.2, 148.2, 147.3, 138.2, 138.0, 130.9, 130.7, 129.6, 129.4, 128.0, 124.9, 123.5, 122.6, 110.7, 71.5, 39.4, 30.6, 29.1, 24.0, 23.0, 14.0, 11.2. MS (EI) *m*/*e* 505 (M^+), 505.6 (calcd). Anal. Calcd for $C_{34}H_{35}NO_3$: C, 80.8; H, 7.0; N, 2.8. Found: C, 80.5; H, 7.0; N, 3.0.

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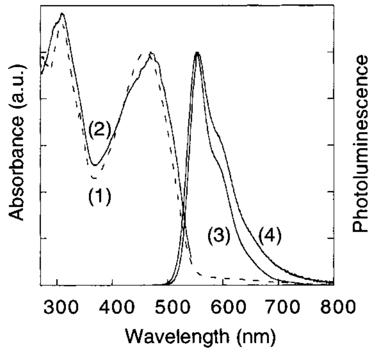

Figure 1. (1) UV−vis absorption spectrum; (2) excitation spectrum at 552 nm emission; (3) PL spectrum under excitation at 459 nm; (4) EL spectrum of the double-layer device of DPAP−PPV.

toluene, and tetrahydrofuran. Content of the *trans*-vinylene-linked structure was estimated to be >99% based on the ^{1}H NMR and IR analysis. Number-average molecular weight of the polymer was 19 000 (M_w/M_n = 1.57). Differential scanning calorimetry gave its relatively high T_g (140 °C). Thermal gravimetric analysis showed no weight loss up to 350 °C and 5% reduction in the polymer weight at ≈400 °C, indicating thermal stability of the polymer and durability for its LED usage.

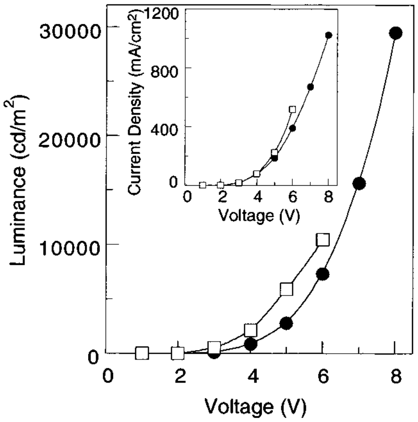

Figure 2. Luminance−voltage characteristics of the double-layer LED device. Inset: current density−voltage characteristics. Cathode metal/Ca (closed circle) or Cs (open square).

UV−vis absorption, PL spectra of the polymer film spin-coated on a quartz substrate are shown in Figure 1. The maximum absorption peaks of the $\pi-\pi_1^*$ transition derived from the PPV backbone and the $n-\pi_2^*$ transition derived from the triphenylamine substitutent are located at 459 and 309 nm, respectively. The band gap of the polymer was estimated to be 2.26 eV from the absorption edge of 542 nm. The polymer film emitted a strong yellow PL emission under the irradiation ascribed to the PPV backbone at 459 nm. Maximum and shoulder peaks of the PL spectrum were at 552 and around 600 nm, respectively. The PL efficiency as the solid-state polymer was 31%,[21] which was twice that of the analogous and well-established poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH−PPV) (15%).[22,23] Interestingly, under irradiation of 309 nm attributed to the triphenylamine moiety, the polymer also showed a strong PL emission at the same wavelength (552 nm), and its PL intensity was higher than that under excitation of the PPV backbone (459 nm) (Figure 1 (2)). This result suggests that a singlet exciton at the triphenylamine moiety effectively transfers to the PPV backbone through the fully conjugated structure and the triphenylamine side chains along PPV might serve as a light-harvesting role of near-ultraviolet light.

Cyclic voltammetry of the polymer coated on indium tin oxide (ITO) glass was measured in a conventional three-electrode cell setup (0.1 M tetrabutylammonium fluoroborate in acetonitrile; versus Ag/AgCl; 100 mV/s; $E_{1/2}$(Fc/Fc$^+$) = 0.54 V). A reversible redox peak was observed at 1.0 V (onset of oxidation peak potential at 0.86 V in the anodic scan), and the cathodic scan exhibited the onset of the reduction peak at −1.1 V without the corresponding oxidation peak. The highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO) energy were electrochemically estimated to be −5.1 and −3.2 eV, respectively;[24] this HOMO level was as high as those of low-molecular hole-transporting materials.[25]

Double-layer LED devices with the configuration as ITO/poly(3,4-ethylenedioxythiophene) (PEDOT):poly(styrene sulfonic acid) (PSS)/the DPAP−PPV polymer/Ca or Cs/Al were fabricated.[26] The DPAP−PPV devices emitted bright yellow light; the EL spectrum showed a maximum emission at 555 nm, which corresponded to the PL spectrum (Figure 1). For the device sealed with a calcium cathode, the turn-on voltage was 3 V with a luminance of 100 cd/m^2, and the device showed a maximum luminance of 29 500 cd/m^2 at only 8 V and a luminous efficiency of 1.1 lm/W (Figure 2). The device with a cesium cathode showed better performance in the low driving voltages (3−6 V) than that with calcium, and the luminance and the luminous efficiency at 3 V were 510 cd/m^2 and 3.0 lm/W, respectively (Figure 2). The maximum luminance of 29 500 cd/m^2 at 8 V with the ITO/PEDOT:PSS/polymer/Ca/Al configuration is almost 2−3 times higher than those of the previously reported LEDs composed of MEH−PPV with the same configuration.[27] We considered that the triphenylamine

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(20) To a xylene (4.9 mL) solution of **3** (0.205 g, 0.406 mmol) and **4** (0.212 g, 0.406 mmol) was added solid potassium *tert*-buthoxide (0.1334 g, 1.19 mmol) at 60 °C. The solution was stirred at 100 °C for 5 h under nitrogen. The reaction mixture was extracted with chloroform. The organic layer was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated. The polymer dissolved in a minimum amount of chloroform was precipitated into methanol to give a bright orange powder (0.182 g, 61%): ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 7.63−6.7 (m, 22H), 4.04−3.40 (m, 7H), 1.87−0.79 (m, 30H). See the Supporting Informaion.

(21) Photoluminescent efficiency of the polymer film was determined relative to a standard film of 9,10-diphenylanthracene dispersed in poly(methyl methacrylate) (Φ = 0.83); Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 7389.

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(26) Thin films of the polymers (80 nm) were prepared by spin coating of 15 g/L 1,2-dichloroethane solution of the polymers filtered through a 0.2-μm PTFE filter before use on an ITO glass pre-spin-coated PEDOT-PSS (60 nm). Thicknesses of the films were measured with a Dektak surface profilometer. A Ca (20 nm) or Cs (ca. 0.5 nm) and Al (150 nm) electrode was deposited, successively, by thermal evaporation under high vacuum (10^{-6} Torr) through a shadow mask (active area: 5.0 × 5.0 mm^2).

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moiety of the DPAP−PPV polymer is more easily doped with the PSS in the buffer layer at the interface of PEDOT:PSS in comparison with the simple MEH−PPV and that more efficient hole injection has been established in the anode interface of the polymer. This was supported by the following experiment: The dichloromethane solution of triphenylamine was vigorously stirred with the aqueous solution of PSS; then, the dichloromethane triphenylamine solution showed a strong visible absorption at 695 nm assigned to a triphenylaminium radical and an ESR signal at the field of $g = 2.003$ ascribed to a nitrogen radical. These devices were fabricated under open air conditions except for vacuum deposition of the metals; we have still not optimized the film thickness and the fabrication (coating) condition such as a solvent speicies and the solution concentration. There remains room to improve the performance, especially the luminous efficiency.

In summary, a novel triphenylamine-substituted and fully conjugated poly(1,4-phenylenevinylene) was synthesized by the Wittig−Horner-type polycondensation. The polymer shows high PL efficiency as a film (31%) and high HOMO energy of −5.1 eV. The simple double-layer devices of the polymer exhibited a very high luminance of 29 500 cd/m^2 under a low driving voltage. The synthetic route will be applicable to introduction of various triphenylamine moieties to the PPV backbones.

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Supporting Information Available: 600 MHz ^{1}H NMR and IR spectrum of the polymer DPAP−PPV (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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