

Synthesis and Characterization of New Blue Light Emitting Alternating Terphenylenevinylene Carbazylenevinylene Copolymer

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Abstract: A new terphenylenevinylene carbazylenevinylene alternating copolymer with the advantage of poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenylene)(PPP) and poly(carbazole) was designed, synthesized and characterized. The polymer structure was confirmed by various spectroscopic analyses and the number average molecular weight (M_n) of the obtained polymer was 7,800. The resulting polymer was thermally stable with high glass transition temperature (T_g) (150 °C), and was readily soluble in common organic solvents. Cyclic voltammetry study revealed that the HOMO and LUMO energy levels of the polymer were 5.37 and 2.47 eV, respectively. The ITO/PEDOT/polymer/Al device fabricated from the polymer emitted bright sky blue light with a maximum peak of around 478 nm. The device showed the maximum brightness of 1,200 nW with a turn-on voltage of 7 V.

Keywords: poly(carbazole), LED, easy hole injection and transporting.

Introduction

The first report in 1990 on the electroluminescence (EL) from poly(*p*-phenylenevinylene) (PPV)¹ triggered a large amount of interest in polymeric light emitting diodes (PLEDs). Since their initial appearance, many improvements have been made in polymer-based devices, including emission across the entire visible spectrum, low drive voltage, good efficiency, and high brightness.²⁻⁵ However, the development of blue-light emitting polymers remains the subject of intense research in both academia and industry due to their potential application in full color flat panel displays.

Poly(*p*-phenylene) (PPP), and its derivatives have also been extensively investigated for light emitting materials because they are thermally and oxidatively stable polymers. PPP derivatives show large band gaps since the aromatic rings are twisted to relieve unfavorable steric interactions in the backbone, which limits the effective conjugation length. Unsubstituted PPP is highly insoluble, limiting the molecular weights and processability. Large, solubilizing substituents may also be incorporated, resulting in improved processability, but this usually exacerbates the steric interactions in the polymer main chain. Thus, PPP derivatives are intrinsically violet-blue emitter to have some difficulties in color

tunability.⁶⁻¹³

Carbazole and its derivatives have attracted extensive interest because of their useful biological activity, and recently, they are expanding their applications as attractive building blocks for the construction of functional materials, such as photorefractive materials, photoconductors, nonlinear optical materials, light emitting materials and hole-transporting materials, because of their inherent electron donating nature, excellent photo conductivity, and unique nonlinear optical property.¹⁴⁻¹⁷

The high efficient LED device, first established by Tang and Vanslyke, was fabricated by incorporating of a hole-and/or electron-transport layer into a multilayer device to balance the charge injection and transport. To facilitate hole injection and transport, triarylamine or carbazole derivatives were employed as the hole-transporting material. Poly(carbazole) derivatives have shown to be excellent hole accepting and hole-transport materials.¹⁸⁻²¹

Recently, we reported the synthesis and characterization of poly(terphenylenevinylene) derivatives and poly(biphenylenevinylene) derivatives with a controlled conjugation length of terphenylenevinylene unit and biphenylenevinylene unit.²²⁻²⁷ They showed good blue electroluminescent characteristics.

In this article, we have synthesized the alternating terphenylenevinylene carbazylenevinylene copolymer, which are composed of poly(carbazole), PPP, and PPV, as shown in

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Scheme I. It is expected that the copolymer have the high efficient EL emission owing to increase of efficient hole injection and transporting ability, and enhancing the thermal stability with high T_g by introducing the carbazole unit.

Experimental

Materials. Triphenylamine, *N*-bromosuccinimide, magnesium powder, triethyl borate, 4,4'-dibromobenzophenone, K_2CO_3 , potassium *t*-butoxide, 4-bromobenzyl phosphonate, bromobenzoyl chloride, aluminum chloride, and tetrakis (triphenylphosphine) palladium(0) were purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) and diethylether were purified by distillation from sodium in the presence of benzophenone. Methylene chloride was purified by distillation after drying over calcium hydride (CaH_2). Other chemicals were used unless otherwise specified.

3,6-Dibenzoyl-9-ethylcarbazole. After 7.2 g (56.32 mmol) of benzoylchloride was slowly added in the stirring of mixture of 5 g (25.6 mmol) ethylcarbazole, 7.5 g (56.32 mmol) of $AlCl_3$ and 100 mL of CS_2 , the mixture was stirred for 24 h. After cooling to room temperature, the mixture was worked up with 100 g of ice and 100 mL of 2 N HCl. After the crude product was extracted with CH_2Cl_2 , the product was purified by recrystallization in the hexane. mp: 182 °C. Yield: 40 %. 1H -NMR ($CDCl_3$, ppm): δ 8.5 (s, 2H), 8.0 (m, 2H), 7.8 (t, 4H), 7.6 (d, 2H), 7.5 (s, 6H), 4.2 (q, 2H), 1.3 (t, 3H) FTIR (KBr) (cm^{-1}): 3020, 2928, 1750, 1350.

3,6-Bis(4-bromophenyl)-1-phenylethylene)-9-ethylcarbazole. After the mixture of 3.2 g (7.44 mol) of phosphonium salt, 0.6 g (24.8 mmol) of NaH and 30 mL of toluene was refluxed for 3 h, it was cooled down to room temperature. After 1 g (2.48 mmol) of 3,6-dibenzoyl-9-ethylcarbazole was added to the mixture, the mixture was refluxed for 35 h. After the reaction was terminated with 50 mL of HCl and 50 g of ice, the crude product was extracted with CH_2Cl_2 . The crude product was purified by recrystallization with hexane. mp: 198 °C Yield : 40% 1H -NMR ($CDCl_3$, ppm): δ 8.1 (s, 1H), 8.0 (s, 1H), 7.9 (s, 1H), 7.4 (m, 17H), 6.8 (m, 4H), 4.2 (q, 2H), 1.2 (m, 3H), FTIR (KBr) (cm^{-1}): 3255, 2928, 1350.

2-Methoxy-[5-(2'-ethylhexyl)oxy]-1,4-benzene diboronic acid (MEHBBA). 2-Methoxy[5-(2'-ethylhexyl)oxy]-1,4-dibromobenzene (40 g, 0.104 mol) was added dropwise to magnesium powders (7.4 g, 0.304 mol) in boiling THF (250 mL). The reaction mixture was refluxed for 2 h and cooled to -70 °C using liquid nitrogen. After the addition of undiluted trimethyl borate (42 g, 0.404 mol), the reaction mixture was stirred for 12 h at room temperature. Then, 300 mL of 2 M H_2SO_4 solution was added. The organic layer was extracted, washed with water, dried over $MgSO_4$ and filtered. The solvent was evaporated off. The residue was recrystallized from ethyl acetate to give white crystals.

mp : 200 °C, Yield : 20%, 1H -NMR ($CDCl_3$, ppm): δ 7.1 (s, 1H), 7.0 (s, 1H), 6.2 (s, 4H), 3.6 (d, 2H), 3.5 (s, 3H), 1.3 (m, 1H), 1.2-1.0 (m, 8H), 0.6-0.5 (m, 6H), ^{13}C -NMR (acetone- d_6 , ppm): 206.4, 205.9, 159.5, 159.2, 119.3, 118.3, 71.7, 56.3, 40.4, 31.4, 30.5, 24.8, 23.6, 14.3, 11.4. FTIR (KBr) (cm^{-1}): 3355, 2928, 2871, 1497, 1387, 1308, 1245, 1202, 1136, 1099, 1059, 885, 777, 718, 645, 554.

Poly[2''-methoxy-5''-(2'-ethylhexyloxy)-3,6-bis(4,4-terphenylene-1-phenylenevinylene)-9-ethylcarbazole] (PMETC). All handling of catalysts and polymerization was done in a nitrogen atmosphere. To a stirred solution of 1-methoxy[4-(2'-ethylhexyl)oxy]benzene diboronic acid (0.46 g, 1.41 mmol), 3,6-bis[4-(4-bromophenyl)-1-phenylethylene]-9-ethyl-carbazole (1 g, 1.41 mmol) in 10 mL of THF and 4 mL of 2 M K_2CO_3 solution in water was added catalysts, $Pd(PPh_3)_4$ (7 mg, 1.5-0.5 mol%). The reaction mixture was heated at 80 °C under nitrogen atmosphere for 8 h. Bromobenzene (0.05 g, 0.318 mmol) was added and then phenyl boronic acid (0.05 g, 0.41 mmol) was added with small amounts of catalysts for end-capping. After 3 h, the reaction mixture was poured into methanol (150 mL) and filtered with glass filter. The residue was dissolved in $CHCl_3$ and washed with waters. After being dried over $MgSO_4$, precipitation was twice repeated with chloroform/methanol. 1H -NMR ($CDCl_3$, ppm): δ 8.1-6.8 (aromatic and vinylic C-H, m, 28H), 4.2 (carbazole N- CH_2 , q, 2H), 3.8 (O- CH_3 and O- CH_2 , m, 5H), 1.8-0.8 (C-H, m, 18H), FTIR (KBr) (cm^{-1}): 3250, 2950, 1350.

Instruments. 1H -NMR spectra data were expressed in ppm relative to the internal standard and were obtained on a DRX 500 MHz NMR spectrometer. FTIR spectra were obtained with a Bomem Michelson series FTIR spectrometer, and the UV-vis absorption spectra obtained in chloroform on a Shimadzu UV 3100 spectrometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly model M590 pump μ -styragel columns of 105, 104, 103, 500, and 100 Å, refractive index detectors, solvent THF). Elemental analysis was performed by Leco Co. CHNS-932. TGA measurement was performed on a Perkin-Elmer series 7 analysis system under N_2 at a heating rate of 10 °C/min. The photoluminescence spectrum was recorded on a Perkin-Elmer LS-50 fluoremeter utilizing a lock-in power meter (Newport 818-SL). Cyclic voltammetry was carried out in a two-compartment cell with a model with platinum electrodes at a scan rate of 10 mV/s against an Ag/Ag^+ (0.1 M $AgNO_3$ in acetonitrile) reference electrode in an anhydrous and nitrogen-saturated solution of 0.1 M Bu_4NBF_4 (tetrabutylammonium tetrafluoroborate) in acetonitrile.

Fabrication of the LED. Poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) for a conducting polymer hole-injection layer was coated on an indium-tin oxide coated glass substrate which had been washed with

water, acetone, and isopropyl alcohol sequentially. A tin polymer film was spin coated (3,000 rpm, 50 s) from a filtered (0.2 μm filter) 1.0 wt% polymer solution in chlorobenzene on a PEDOT layer (800-1,100 Å). An aluminium electrode was deposited on top of the device at a high vacuum (1,300 Å, below 1×10^{-5} Torr). Wires were attached to the respective electrodes with a conductive epoxy adhesive. All fabrication steps were performed in clean room conditions. Measurements were done at room temperature in air.

Results and Discussion

The synthesis of the monomer and polymer is outlined in Scheme I. The monomers were prepared by a Fiedel-crafts acylation reaction and Wittig reaction of (4-bromobenzyl) triphenylphosphonium bromide with 3,6-dibenzoyl-9-ethylcarbazole. The polymerization was carried out using a typical Suzuki coupling reaction with good yield. After the polymerization, the end-capped reaction of the bromine end group and boronic acid end group, which both hamper the thermal stability and efficiency of PL, were accomplished by phenyl boronic acid and bromobenzene, respectively. The polymer structure shown was consistent with the elemental analysis and the spectroscopic data from $^1\text{H-NMR}$ and FTIR. Figure 1 showed $^1\text{H-NMR}$ and IR spectra of PMETC. In the IR spectrum, O-H stretching of boronic acid at 3500 cm^{-1} and aromatic C-Br stretching at 1065 cm^{-1} were

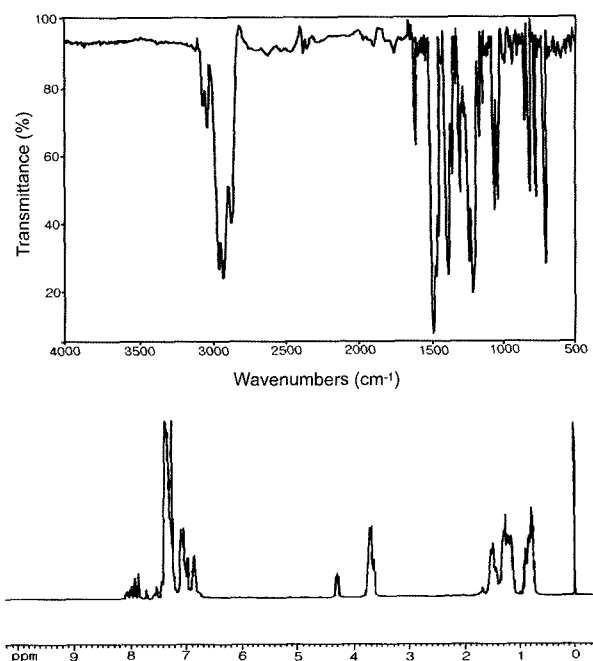
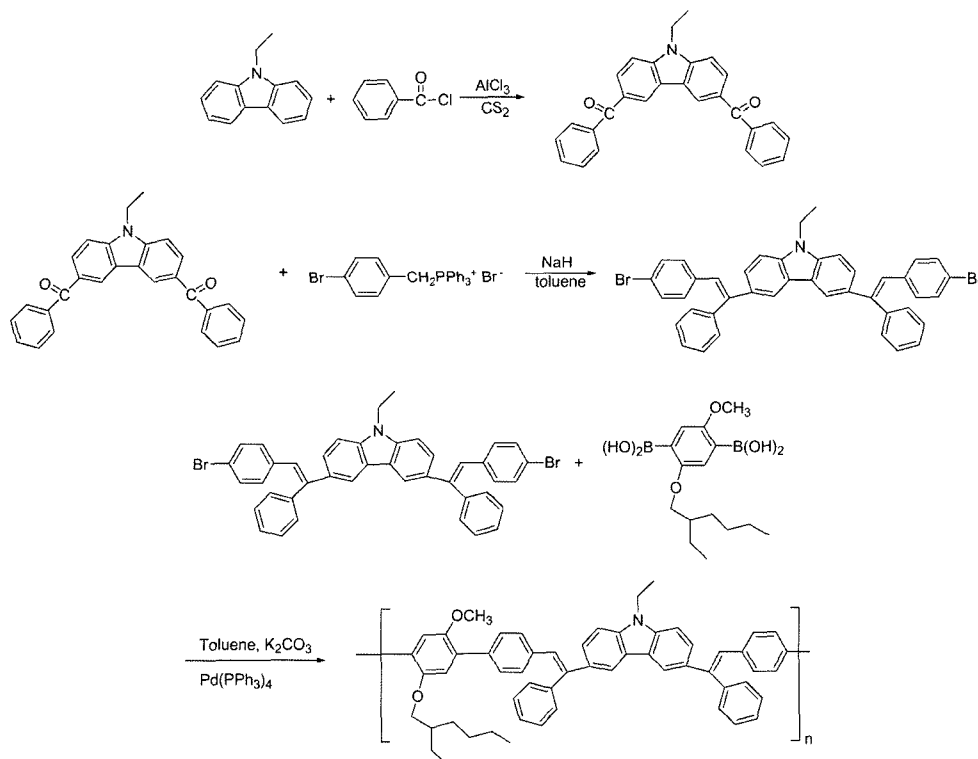


Figure 1. IR and $^1\text{H-NMR}$ spectra of obtained copolymer.

disappeared. In the $^1\text{H-NMR}$ spectrum, the vinylic proton peak appeared at around 6.5-7.0 ppm with aromatic proton peaks. Methoxy and oxymethylene proton peaks showed at

Scheme I



around 3.8 ppm. All other peaks showed good correspondence with the chemical structure of polymer. The obtained polymer was readily soluble in common organic solvents such as chloroform, dichloromethane and toluene. The number average molecular weight (M_n) and polydispersity index of polymer is 7,800 and 2.1, respectively, which is sufficiently high to be considered as a EL material. The thermal stability of the polymer was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) under a nitrogen atmosphere at a heating rate of 10 °C/min. Figure 2 shows TGA and DSC curve of the polymer. The polymer has onset degradation temperature above 380 °C, and 5% weight loss was observed at above 400 °C. The glass transition temperature (T_g) of PMETC showed at 150 °C. It is known that materials with high glass transition temperature as the active emissive layer can provide the device longevity. Figure 3 shows the optical absorption and

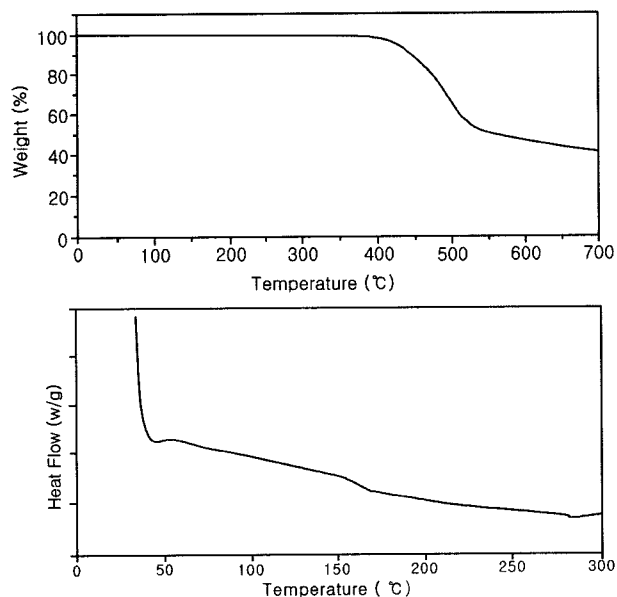


Figure 2. TGA and DSC thermogram of obtained copolymer.

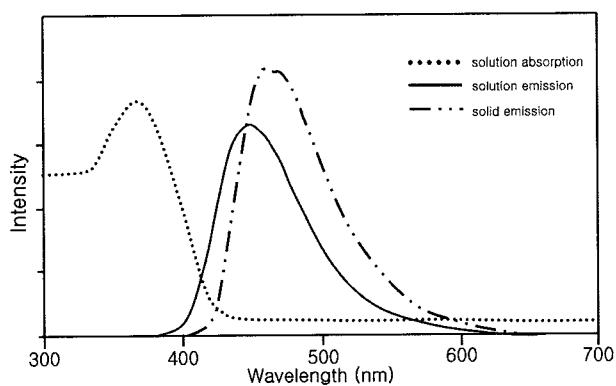


Figure 3. UV-absorption and PL emission spectra of copolymer (chloroform solution, 10^{-4} mol/L).

photoluminescence spectra of a dilute solution of the polymer in chloroform. The maximum absorption of polymer showed at 362 nm. The band-gap energy of the new polymer estimated from extrapolation of the low energy absorption spectra was about 2.90 eV. The PL spectrum was recorded with an excitation wavelength corresponding to the absorption maximum wavelength of the polymer. The polymer emitted strong blue fluorescence under ultraviolet irradiation in a chloroform solution ($\lambda_{max}=456$ nm) and in the film ($\lambda_{max}=473$ nm). The red shift relative to the solution is attributed to packing effects in the local geometry of the polymer.²⁸ The electrochemical behavior of the obtained polymer was investigated by cyclic voltammetry. Upon the anodic sweep, the polymer exhibited with a formal oxidation potential (E°) at + 0.97 eV. Based on the onset potential for the oxidation and reduction, the HOMO and LUMO energy level of the new polymer was estimated to 5.37 and 2.47 eV, respectively. The low HOMO level may be due to introduction of carbazole group with electron donating nature, which leads to a significant increase in hole injection and transport ability.²⁹

In order to investigate the electroluminescent property of the polymer containing carbazole and terphenylene, ITO/PEDOT/polymer/Al device was fabricated and evaluated. Figure 4 shows the electroluminescence spectrum of ITO/PEDOT/polymer/Al device. The EL spectrum of the device had a maximum peak at 478 nm with a shoulder peak at around 550 nm corresponding to greenish blue light. The EL spectrum shows a red shift compared to the PL and a significant spectral broadening. The red shift in the EL spectrum is attributed to the fact that electroluminescent excitons are generally adequately thermalized compared to photoluminescent excitons as a result of their different modes of generation. The tailing in the long wavelength region is largely due to defects in the emissive polymer layer which

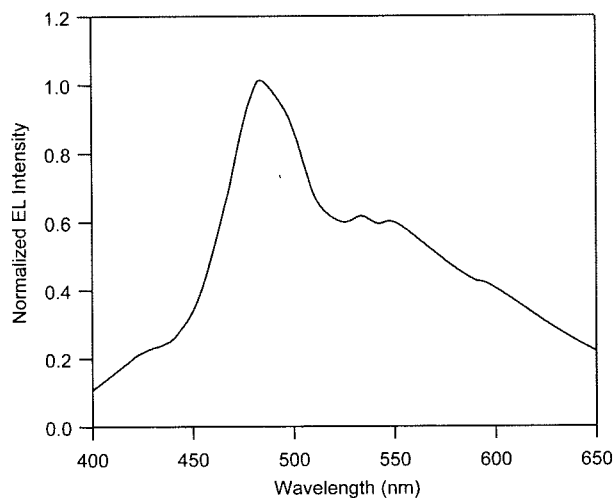


Figure 4. Electroluminescent spectrum of ITO/PEDOT/polymer/Al device.

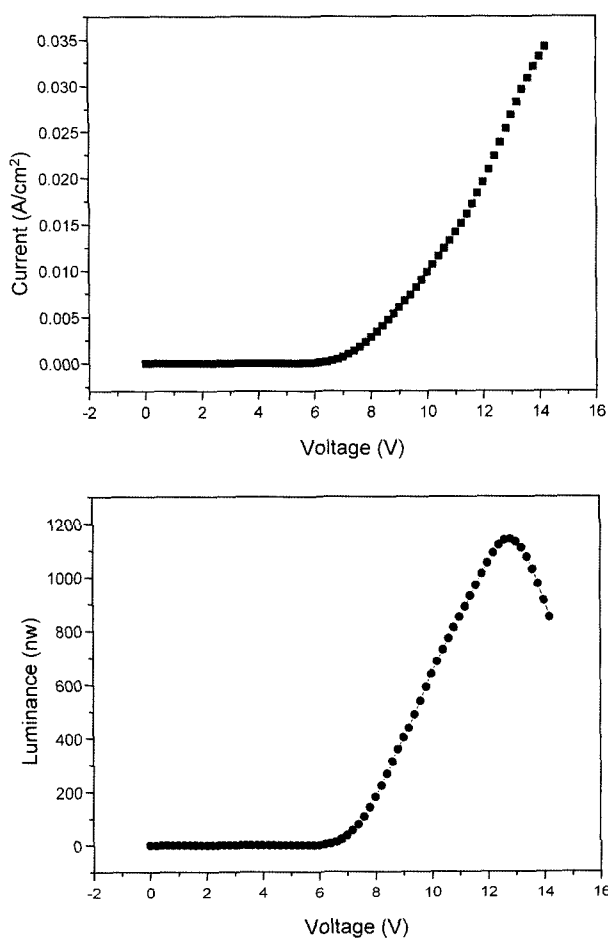


Figure 5. Current-voltage and brightness-voltage characteristics of ITO/PEDOT/polymer/Al device.

act new recombination centers in which excitons radiatively decay giving emissions different from those given by excitons decaying on the pristine polymer main chain.³⁰⁻³² Figure 5 represents the voltage-current (I-V) and voltage-brightness curve (L-V) characteristics of device. The current and light arise at almost the same voltage (7 V), indicating a balance of hole and electron injection. The maximum brightness of the device was 1,200 nW at 13 V and 35 mA/cm².

Conclusions

The alternating terphenylenevinylene carbazolevinylene copolymer, which are composed of poly(carbazole), PPP and PPV, is synthesized by Suzuki coupling reaction with 3, 6-bis[(4-bromophenyl)-1-phenylethylene]-9-ethylcarbazole and 1-methoxy[4-(2'-ethylhexyl)oxy]benzene diboronic acid. The polymer showed high thermal stability with high T_g (150°C). The obtained polymer showed the low HOMO level due to the introduction of carbazole group, which leads to a significant increase in hole injection and transport ability.

The maximum brightness of the device was 1,200 nW at 13 V and 35 mA/cm².

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